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Development of a Continuous Monitor for Detection of Toxic Organic Compounds

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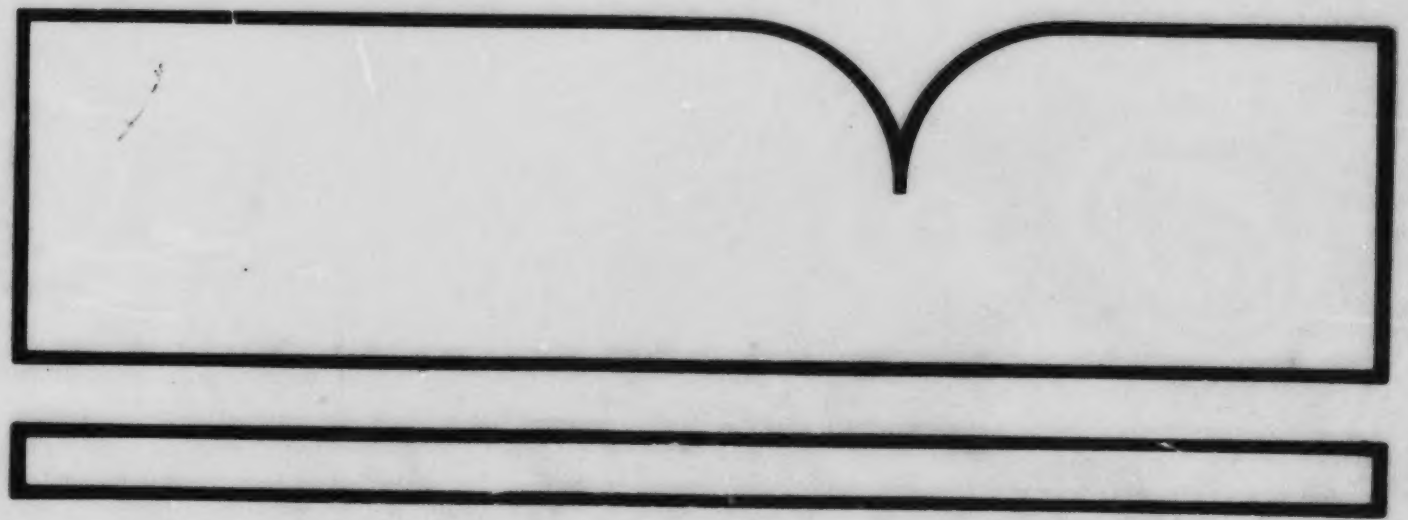

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16. ABSTRACT

The goal of the present program was the design, construction, and delivery to EMSL/RTP of a small continuous monitor for benzene and other organic compounds based upon Tunable Atomic Line Molecular Spectroscopy. The most limiting design factor was found to be the detection limit of the instrument. To improve this limiting factor, the following new developments were investigated: a) a new light source with high intensity and high stability that can excite the spectra of many elements; b) a negative feedback circuit to further control light source stability; c) instrumentation for double beam operation; d) a technique for more rapid location of atomic lines that match molecular absorption. These developments have improved the sensitivity of the TALMS benzene monitor by a factor of 100 to a detection limit of 3 ppm-v benzene. The instrument that was delivered to EMSL/RTP is compact in size (41 inches in length) and weight (75 lbs.) and requires a modest amount of power (125 watts). It was supplied with a permanent magnet of field strength 7 kG (0.7T) and utilizes the Hg 253.6 nm line. It can be equipped with a monochromator and is designed to interface with a Hewlett-Packard 85 computer. A cryogenic concentrator was designed for use with this instrument.

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DEVELOPMENT OF A CONTINUOUS MONITOR FOR DETECTION OF TOXIC ORGANIC COMPOUNDS

by

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems for air, implementation of agency-wide quality assurance programs for air pollution measurement systems, and supplying technical support to other groups in the Agency including the Office of Air, Noise, and Radiation, the Office of Pesticides and Toxic Substances, and the Office of Solid Waste and Emergency Response.

Analysis of organic compounds in the atmosphere is a difficult task requiring a variety of analytical techniques to ensure that identification and quantification are valid. The environmental analyst requires methods that are precise, accurate and easy to implement. This study is concerned with the development of a new instrument which utilizes the information available in the high resolution absorption spectra of organic compounds in the ultraviolet and visible regions. The use of this instrument in the analysis of organic compounds may greatly improve the ability of the analyst to produce valid results.

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ABSTRACT

This research and development program was undertaken by the Lawrence Berkeley Laboratory to investigate the application of a new analytical technique called tunable atomic line molecular spectroscopy (TALMS) to the detection and monitoring of benzene and other volatile organic molecules of concern to the Environmental Protection Agency. Previous studies under Interagency Agreement EPA-IAG-80-D-X-1014, which was completed in September, 1981, have led to the design, construction, and delivery to the Environmental Monitoring Systems Laboratory at Research Triangle Park, NC (EMSL/RTP) of a laboratory TALMS spectrometer. The goal of the present program was the design, construction, and delivery to EMSL/RTP of a smaller continuous monitor for benzene and other organic compounds.

The most limiting design factor was found to be the detection limit of the instrument. To depress this limiting factor, the following areas were investigated: intensity of light source line; location of atomic line relative to molecular absorption feature; light source noise; and magnetic field direction.

New developments in TALMS instrumentation that resulted from the investigation of these factors include:

a. a new light source with high intensity and high stability that can excite the spectra of many elements;
b. a negative feedback circuit to further control light source stability;
c. instrumentation for double beam operation;
d. a technique for more rapid location of atomic lines that match molecular absorption;

These developments have improved the sensitivity of the TALMS benzene monitor by a factor of 100 to a detection limit of 3 ppm-v benzene. Cryogenic trapping procedures, especially adapted to the monitor, were also used to improve sensitivity. Additional concentration factors of 100 to 1000 can be achieved using these procedures. Estimates of linear dynamic range, precision, interferences, and detection limits for benzene are presented. Approximate detection limits for formaldehyde and phenol of 1 ppm-v were also determined.

The instrument that was delivered to EMSL/RTP is compact in size (41 inches in length) (104 cm) and weight (75 lbs.) (28 kg) and requires a modest amount of power (125 watts). It was supplied with a permanent magnet of field strength 7 kG (0.7T) and utilizes the Hg 253.6 nm line. It can be equipped with a monochromator and is designed to interface with a Hewlett-Packard 85 computer. A cryogenic concentrator was designed for use with this instrument.

This report was submitted in fulfillment of Interagency Agreement EPA-IAG-AD-89-F-2-A008 by the Lawrence Berkeley Laboratory under the

sponsorship of the U.S. Environmental Protection Agency. Work was completed on September 30, 1982.

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SECTION 1

INTRODUCTION

Without dependable chemical analysis the environmental protection regulatory process cannot be effective. Yet, the complexity of environmental analytical problems is great both in terms of the variety of compounds that must be detected and in terms of the complex matrices that must be analyzed. The monitoring of trace amounts of organic compounds is especially difficult. At low concentrations many ambient air samples contain hundreds - if not thousands - of different organic compounds. An analytical technique that is dependable when dealing with this type of sample must include a method for uniquely identifying these many possible species. Present approaches almost always involve some type of chromatographic separation that depends upon small differences in solubility or volatility. It follows that shortcomings in present chromatographic methods impose similar limitations on almost all techniques now used to determine trace organics. In addition, this common origin of methodologies makes it impossible to confirm an analysis with a totally independent method, which is a very important part of quality assurance.

Studies carried out at the Lawrence Berkeley Laboratory under a previous Interagency Agreement have demonstrated that another technique, not dependent on chromatographic separations, shows promise of being a successful new method for the determination of trace organic compounds in ambient air [1]. This technique is called tunable atomic line molecular spectroscopy (TALMS) [2]. As a part of the previous study a laboratory TALMS instrument was constructed and delivered to Environmental Monitoring Systems Laboratory in North Carolina.

TALM Spectroscopy consists of splitting a source atomic emission spectral line by means of a magnetic field (Zeeman effect) and making a differential absorption measurement between one Zeeman component that has been magnetically tuned to an analyte rotational-vibrational, absorption line and the other Zeeman components. The difference in polarization between Zeeman components permits the matching and nonmatching wavelengths to be alternately selected and the differential absorption measured very rapidly with an electrooptical device called a variable phase retardation plate. Since the wavelength separation between Zeeman components is small, a signal will only be obtained if the analyte contains a sharp absorption feature, i.e. less than 3 cm^{-1} bandwidth. This process is illustrated in Figure 1. The upper portion of this figure is a high resolution scan of the absorption spectrum of chlorobenzene in the region of 253.6 nm. The lower portion displays the Zeeman components that result when the Hg 253.6 nm line is split by a magnetic field (parallel Zeeman effect) at a field strength of ca. 12 kG (1.2T). Since the absorption is different at the two different Zeeman components, a differential TALMS signal will be detected.

Thus, the TALMS signal depends upon a high-resolution (>500,000), ultraviolet, absorption measurement and should be free of the limitations of chromatographic separations. The high resolution capabilities of the technique have been demonstrated in a recent publication on formaldehyde [3].

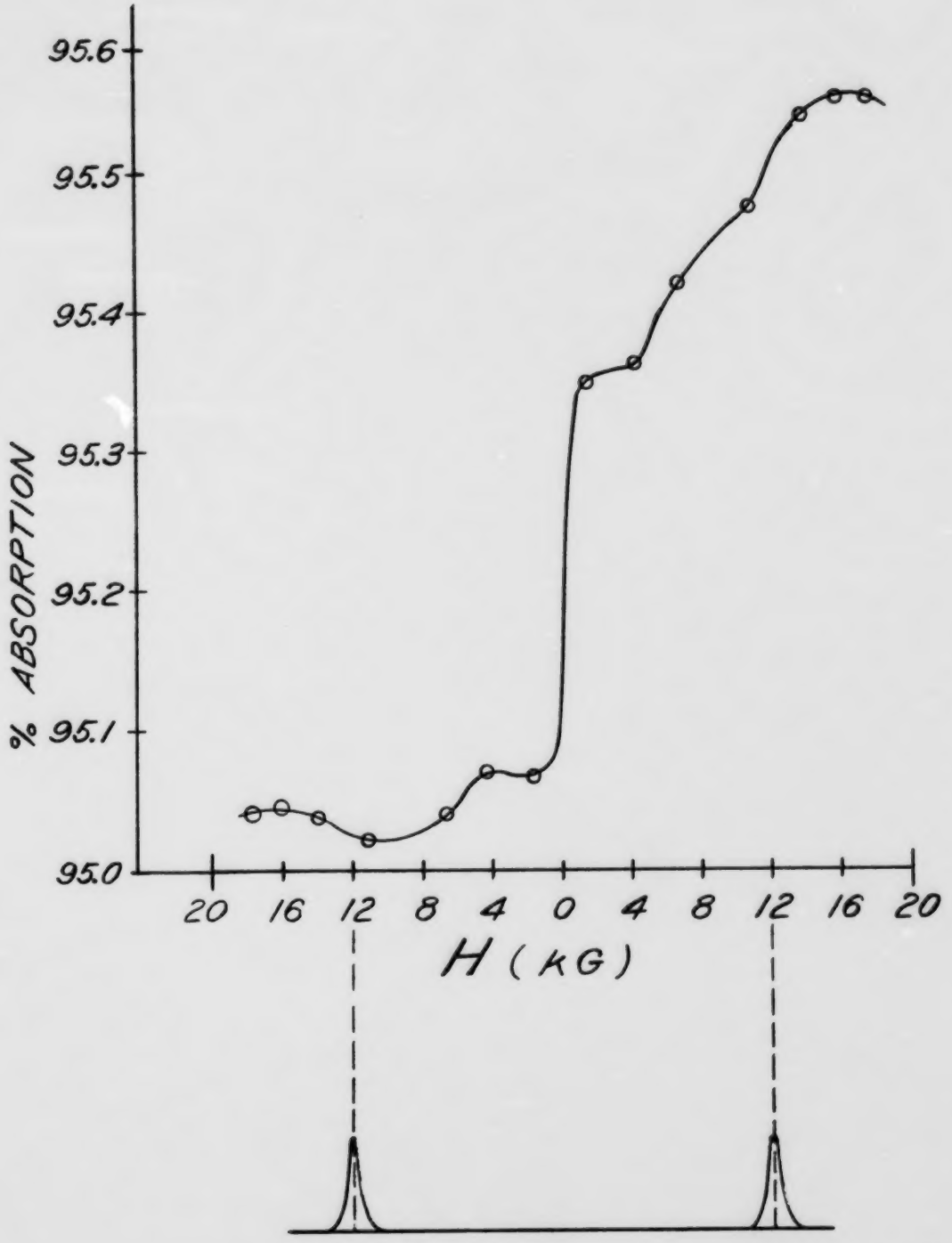

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Figure 1. TALMS detection of chlorobenzene using parallel Zeeman effect and the Hg 253.6 nm line.

One remarkable feature of TALMS is its essential freedom from background interference. Since the wavelength separation between the Zeeman components is typically 0.04 nm, any particle scattering or semi-continuous absorption will affect both components equally. Therefore, the differential absorption measurement will remove this interference from the signal. Hence, this type of interference, which is a major problem with most spectroscopic methods, does not effect the TALMS measurement. The limitations on the sensitivity of TALMS in ideal situations are essentially the same as those on ultraviolet absorption spectroscopy.

In the previous study (1, 2) TALMS signals were detected for benzene and chlorobenzene using the Hg 253.6 nm line. The objective of the present study is to design and construct a continuous monitor for benzene and other toxic organic compounds in ambient air. In the design of such an instrument a number of factors are very important. These include instrument size, complexity of operation, sensitivity, interferences, precision and accuracy, and cost. Perhaps the most important of these factors is sensitivity (lower limit of detectability) since benzene occurs in ambient air at the part per trillion to part per billion by volume level [4]. This report describes the development of techniques that have led to a great improvement in TALMS instrumental performance over the previous system. The instrument that resulted incorporates these techniques and is designed to be interfaced to a HP-85 micro processor. This combination allows basic data to be stored over a variety of periods of time.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

This work has been primarily concerned with the design and construction of a monitor for benzene and other toxic organic compounds that utilizes the TALMS technique. The most critical performance parameter in the design and construction of the monitor has been the detection limit. The following areas have been investigated to improve this parameter:

a. Light source construction and operation
b. Effects of magnetic field direction
c. Double beam operation
d. Negative feed back control of the light source
c. Optimization of matching the atomic emission lines to the molecular absorption feature
f. Cryogenic trapping.

As a result of these experiments, it was possible to incorporate many effective modifications into a prototype instrument and improve the lower limit of detection by a factor of 100 over that of the previous laboratory instrument. The resulting detection limit for benzene (~3 ppm-v) should be sufficient for monitoring urban air near sources or chemical waste sites. An additional detection limit improvement by a factor of 100 - 1000 was demonstrated using cryogenic trapping. This sensitivity (~0.3 ppb) should be sufficient to monitor most ambient urban environments. This TALMS monitor has been constructed and delivered to the EPA. It is as compact as possible without sacrificing the performance features developed for the laboratory model (weight 75 lbs; length 41 inches). It utilizes the mercury 253.6 nm line and a double beam optical system. Procedures for calibrating this instrument both in the field and in the laboratory have been developed; so also have methods for verifying the performance of the cryogenic trapping system. Any further improvements in the detection limit will have to come from utilizing more intense absorption features in the analyte absorption spectrum. In the process of these investigations, phenol and formaldehyde were also detected and approximate detection limits established. The detection of these molecules points the direction of future work with this technique.

The use of this type of instrumentation for monitoring more organic molecules should be investigated. Operation of the light source with a greater variety of elements should be tested both to allow the detection of additional molecules and to improve the sensitivity for molecules that have already been detected. Calibration and quality assurance procedures should be developed that allow this technique to be compared with other methods. Efforts should be expended to further reduce size and weight with the goal of a portable instrument. Methods of simplifying operating procedures should receive attention, and aids in the form of operation and repair manuals should be generated.

SECTION 3

IMPROVING INSTRUMENT PERFORMANCE

As mentioned previously, one of the requirements of a monitor for benzene in ambient air is a very low detection limit (ca. ppt to ppb-v). Accordingly, improvements were made in several different areas that resulted in improvement of instrument detection limit. Each is described below.

MAGNETIC FIELD DIRECTION

In order to optimize TALMS for a particular molecule, it is necessary to determine a detailed line profile of the molecular absorption feature over the region scanned by the atomic line, i.e. a high resolution absorption spectrum. This can best be accomplished with TALMS equipment by measurements of I/I_o for the σ^+ and σ^- Zeeman components. A curve of this type for chlorobenzene has already been displayed in Figure 1. The corresponding curve for benzene is displayed in Figure 2. The Zeeman pattern for the Hg 235.6 nm line observed perpendicular to the direction of the magnetic field also is shown at the bottom of this figure.

There are two orientations of the light emission direction with respect to the magnetic field direction that can be used in the TALMS system, parallel and perpendicular. The parallel is illustrated in Figure 1 and the perpendicular in Figure 2. The advantage of using the parallel Zeeman configuration for measuring line shapes can be seen by comparing components obtained in the two field directions for the Hg line. (Compare Figures 1 and 2.) The parallel Zeeman configuration results in two circularly polarized components (σ^+ and σ^-) whose separation can be increased by applying larger magnetic fields. (For other atomic lines more than two components could be produced.) Hence, the transmission of each of these components through a cell containing the species of interest as a function of field strength, reveals the absorption profile of the molecule. As seen in Figure 2, the perpendicular Zeeman component generally consists of an unshifted π component of one polarization and two shifted σ components of different polarization. It is not possible to isolate the σ components with a retardation plate because their polarization properties are the same. Hence, it is very difficult to determine molecular line shapes using the perpendicular configuration. The resolution of the spectral scan obtained with the parallel Zeeman configuration will be determined by the line width of the emission line (ca. 0.06 cm^{-1}) [5]. For the mercury line at 253.6 nm this corresponds to a resolution ($\lambda/\Delta\lambda$) of ca. 700,000.

The reason it is possible to monitor both benzene and chlorobenzene with the same mercury line (253.6 nm) can be seen by comparing Figures 1 and 2. The structure of the chlorobenzene absorption is such that about half of the π component is absorbed in one polarization and one of the two σ components is absorbed in the other polarization. Since about the same amount of absorption occurs in both polarizations, the signal resulting from measuring the difference in polarization intensities will not be very sensitive to the amount of chlorobenzene in the light path. However, the

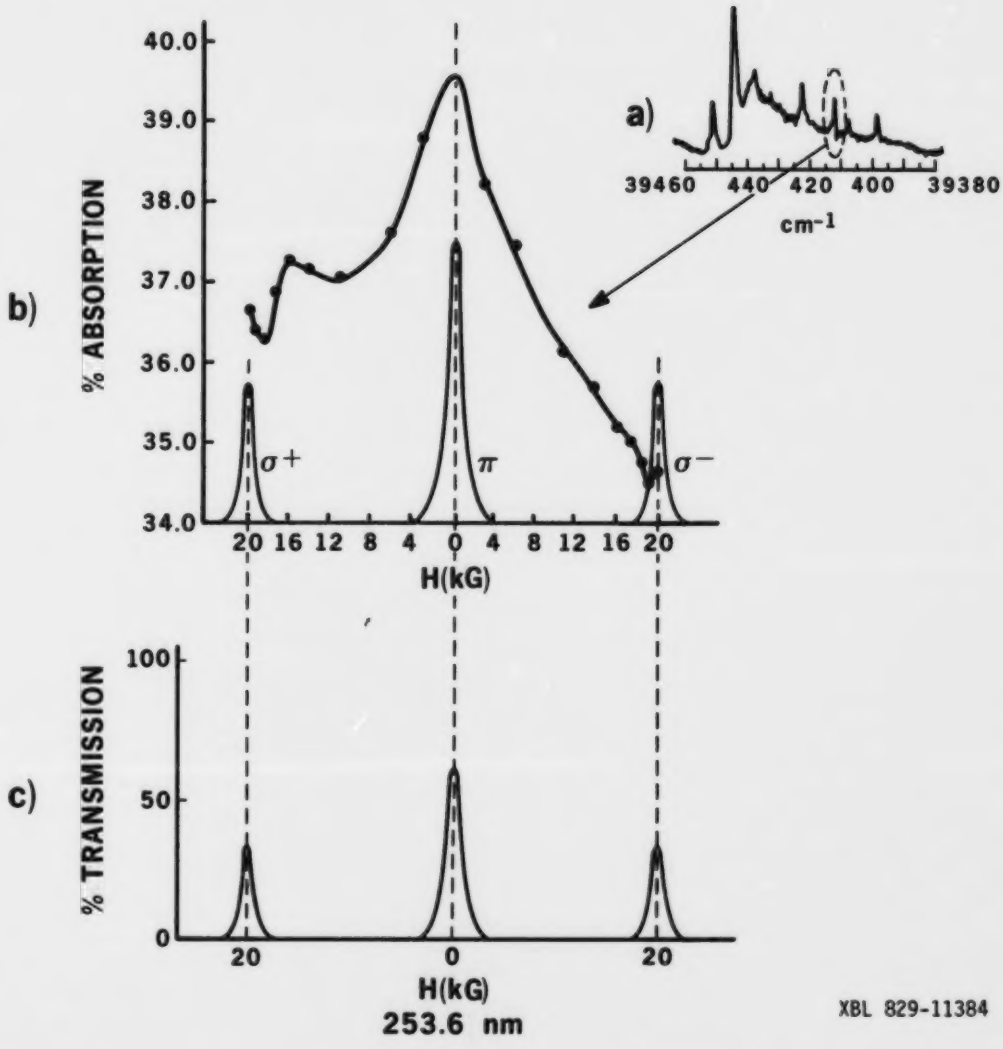

Figure 2. High resolution absorption spectrum of benzene and Zeeman split Hg 253.6 nm line:

a) Absorption spectrum [12].
b) Zeeman scan and Hg Zeeman pattern of region dotted in (a).
c) Zeeman components transmitted by benzene at 2.0 T (20 kG).

difference in intensities between the two σ components obtained from the parallel Zeeman configuration is very sensitive to the presence of chlorobenzene. This is illustrated in Figure 3 which displays the shape of the chlorobenzene absorption feature (solid line), the TALMS signal in parallel configuration (dashed line to the right of 0 kG), and the TALMS signal in perpendicular configuration (dashed line to the left of 0 kG). It is obviously better to use the parallel field orientation for chlorobenzene.

On the other hand, the benzene molecule absorbs the central π component much more strongly than the shifted σ components (see figure 2). For this reason benzene will be monitored if the perpendicular Zeeman configuration is used, and the system will be relatively insensitive to benzene if the parallel Zeeman configuration is used. The relative strengths of the TALMS signals from the two configurations is shown in Figure 4. (Again the shape of the absorption is represented by the solid line, the TALMS signal in parallel configuration by the dashed line to the right of 0 kG, and the TALMS signal in perpendicular configuration by the dashed line to the left of 0 kG.) It is also obvious that higher signals for benzene and chlorobenzene are obtained at higher magnetic field strengths.

The relative strength of TALMS signals from parallel and perpendicular Zeeman configurations depends upon the position of the atomic line with respect to the molecular absorption feature and the shape of the feature. Four basic situations exist (see Figure 5). The unshifted atomic line (dotted line on the Figures) may be on the peak of the absorption (case A), may lie to the left of the peak (case B), to the right of the peak (case C), or may be in a region of no structure (case D). The benzene situation corresponds to case (A) and the chlorobenzene situation to case (B). The wavelength interval involved in TALMS measurements is very small, hence, case (D) is much more probable than (A), (B), or (C). When case (D) occurs there is background correction but no signal. It is apparent from these considerations that the strength of the TALMS signal is very dependent on the molecular band shape and the wavelength of the atomic line.

The structure of the absorption feature can be inferred by monitoring the strength of the TALMS signal as a function of field using the parallel Zeeman configuration. This is simplier than the I/I_o measurement mentioned earlier. If, as the field is changed, one Zeeman component passes through the absorption feature and the other does not, the molecular structure is traced out directly (see Figure 1 as an example). Formaldehyde is another example of this kind that has already been reported [3]. If, on the other hand, changing the field strength scans both components through regions that contain molecular structure, complex patterns may result. Figure 6, (obtained for SO_2), [6] is one such example. This type of pattern would result if the unshifted atomic line fell between two SO_2 absorption peaks. In order to be certain of the structure in this case an I/I_o measurement should be made.

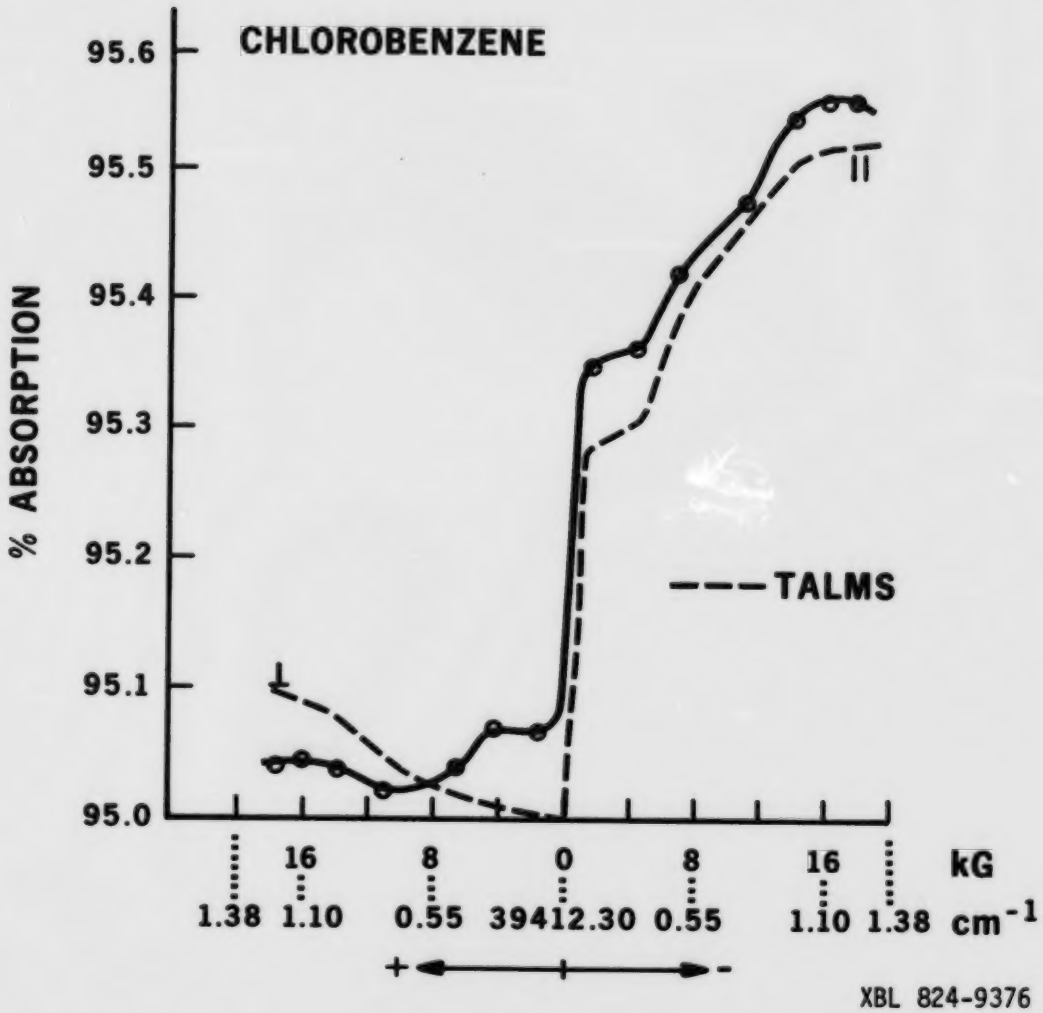

Figure 3. TALMS signals for chlorobenzene as a function of magnetic field strength and orientation.

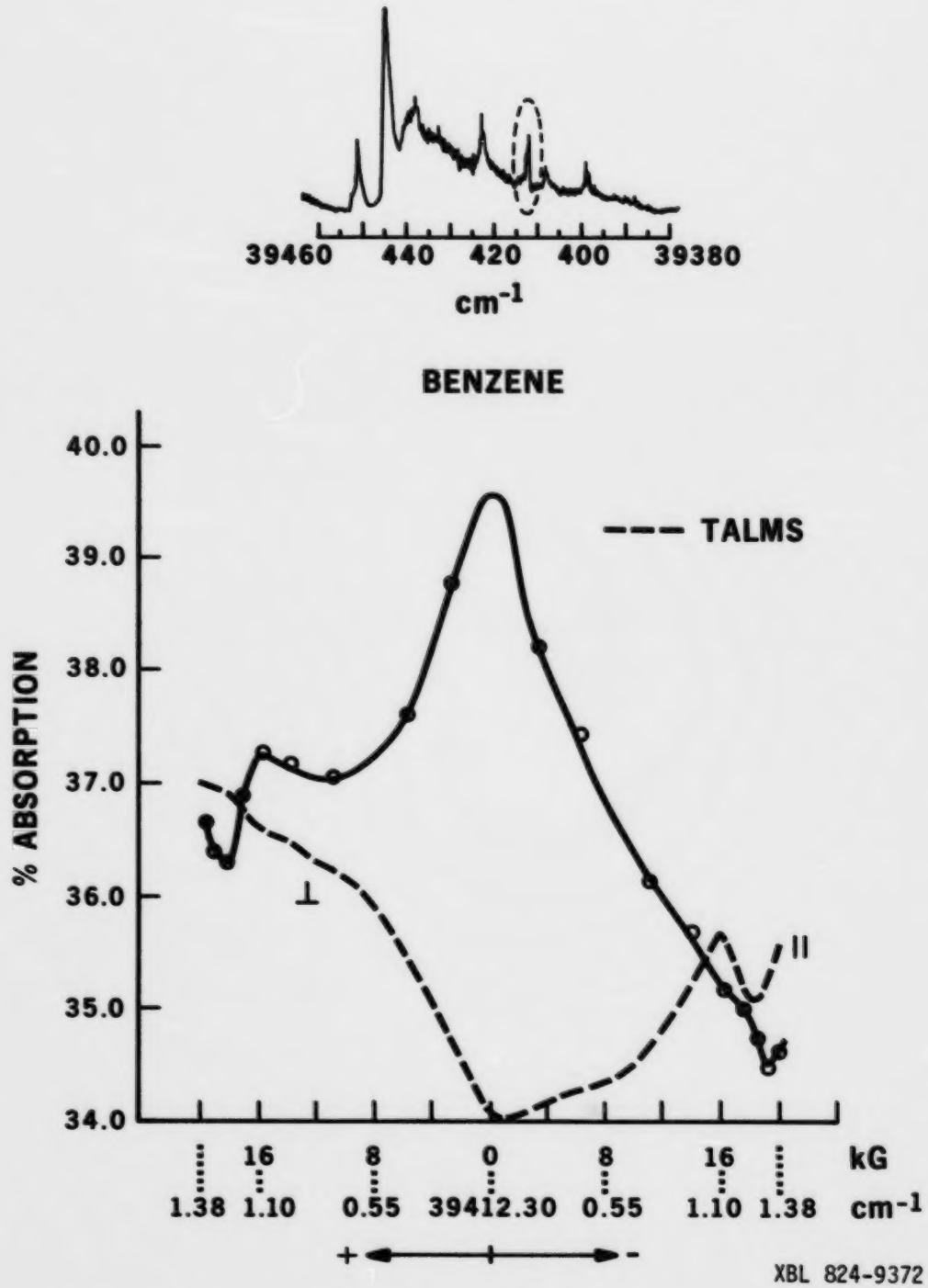

Figure 4: TALMS signals for benzene as a function of magnetic field strength and orientation.

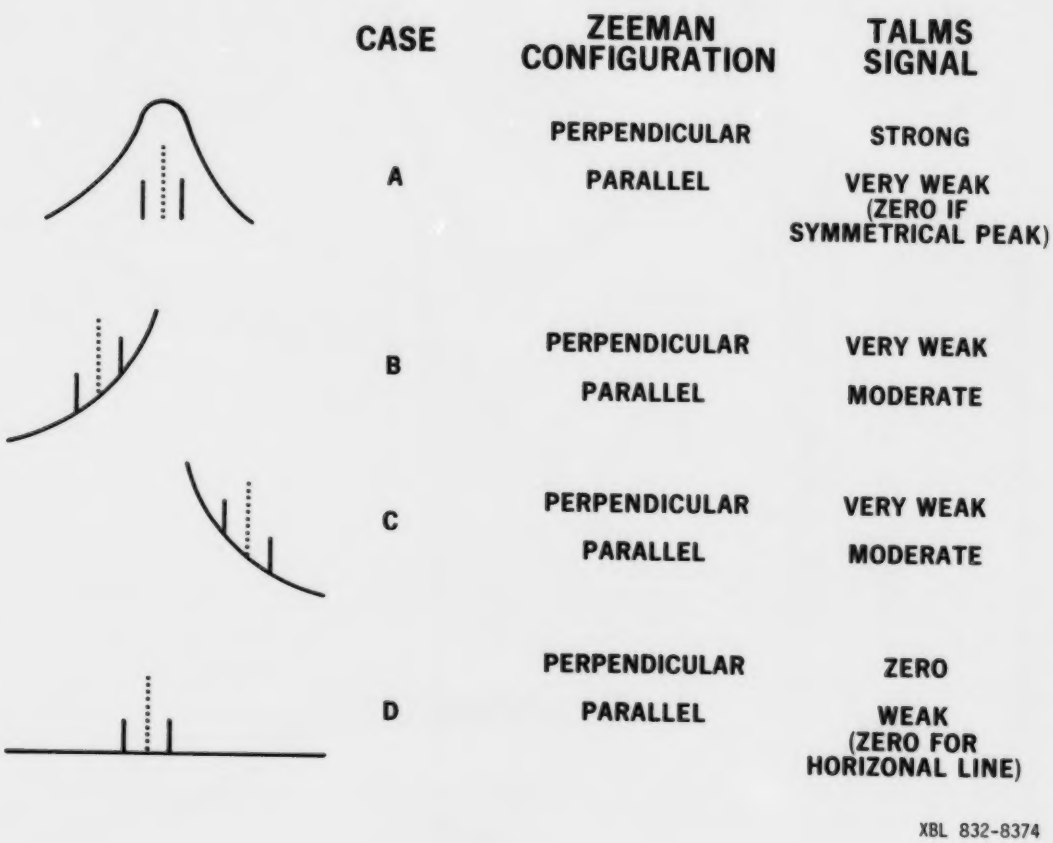

Figure 5. TALMS signals resulting from different Zeeman configurations and absorption features.

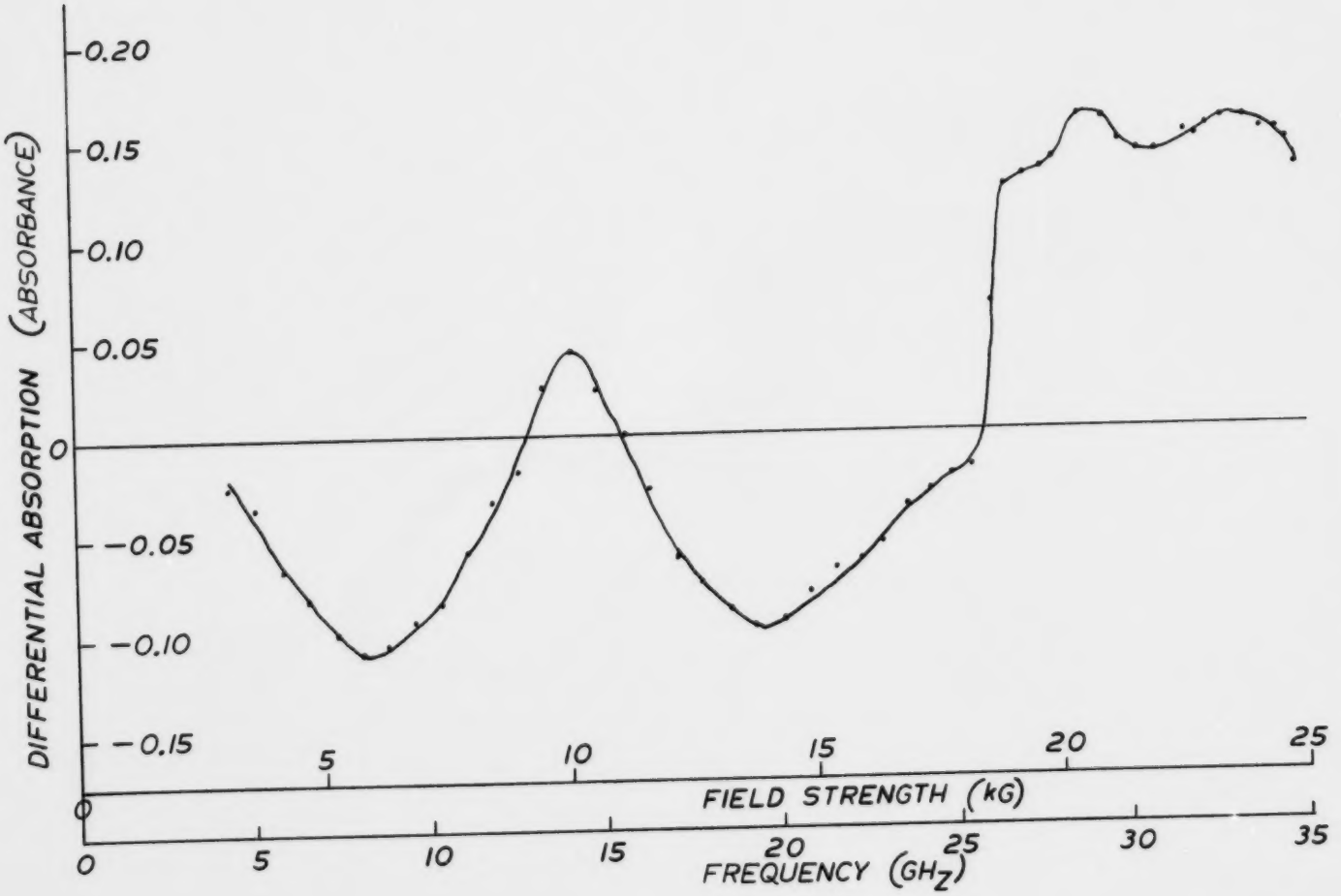

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Figure 6. TALMS signal for SO_2 as a function of magnetic field strength.

LIGHT SOURCE DEVELOPMENT

In any analytical instrument the ultimate limit of detection is frequently determined by the noise of the instrument. In spectrophotometric instruments, e.g. atomic absorption spectrometers, ultraviolet-visible spectrophotometers, and TALMS; the source of noise can be grouped into three categories [7].

1) 0% Transmission Noise - obtained when instrument is operational but with no light passing through the the system. It consists of:
Environmental Noise which arises from the surroundings and occurs because conductors in the instrument can act like antennae capable of picking up electromagnetic radiation. Sources of this type of noise include such things as brushes in electrical motors, elevators, gasoline engines, and, at high frequencies, radio and TV signals. Environmental noise can also result from vibrational effects that result in light leaks and temperature effects that cause fluctuations in the transducer and amplification systems.
Johnson Noise which is the result of thermal motion of electrons in resistive circuit elements. This source of noise is a much greater problem in infrared detection systems than in the ultraviolet and visible systems because of intrinsic differences in the detectors.

2) Shot Noise - which results whenever electrons must cross a junction such as the transfer between dynodes of a photomultiplier tube. This noise is caused because the number of electrons that make the crossing is not the same with each event but have a statistical distribution that obeys the laws of quantum mechanics. The higher the signal level, the less the error caused by shot noise [8]. (The intensity reaching the detector should always be large enough that errors caused by dark current from the photomultiplier can be neglected).

3) Flicker Noise - which is caused by fluctuations in the light source. Measurements on atomic absorption systems indicate this type of noise is present at levels of 0.25 % of the signal from hollow cathode light sources [9].

In the development of the TALMS instrument all of these sources of noise were investigated. Construction of a high-intensity, low-noise light source can make shot noise and flicker noise small compared to 0% transmission noise.

There is a severe constraint on light sources used in TALMS instruments. They must be as small as possible to fit between the poles of a magnet. A smaller light source permits the use of a smaller pole gap. As shown in Figure 4, for benzene, the higher field strengths yield greater TALMS signals. The light source that has been developed to operate within this constraint is pictured in Figure 7. The housing is a commercially available vacuum flange (Varian conflat, nonrotatable). Conical shaped iron pieces have been bolted to either side of this flange to serve both as walls of the discharge chamber and as magnetic pole pieces (see Figure 8). This assembly

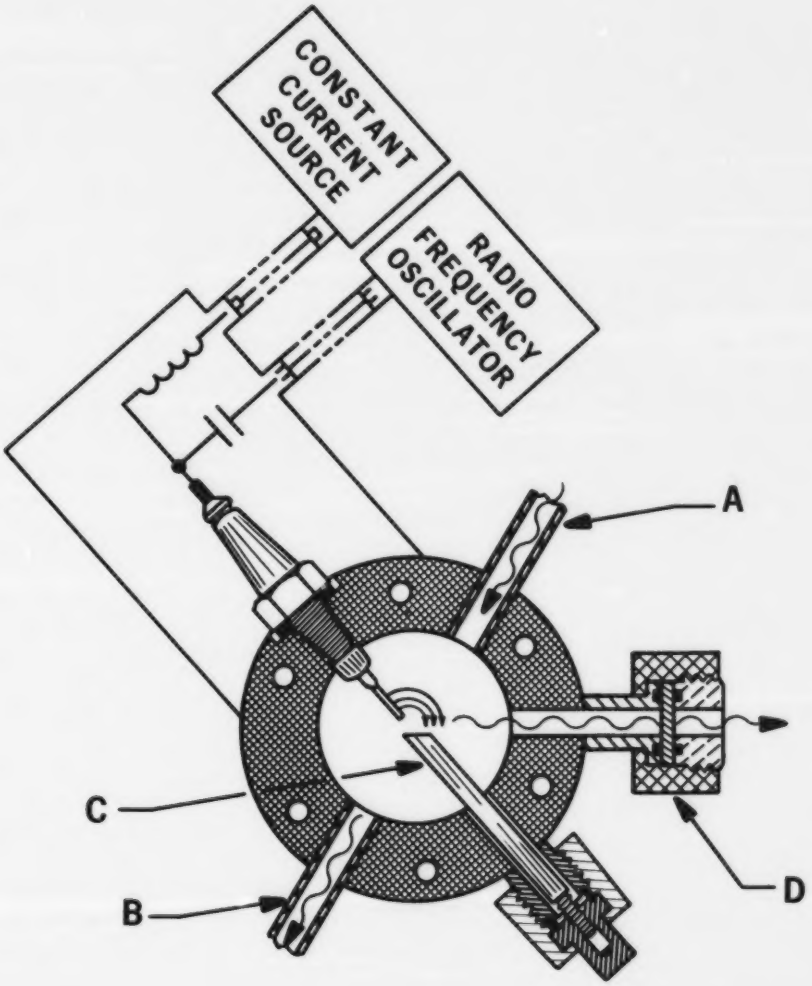

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Figure 7. Magnetically contained discharge lamp. The carrier gas enters port A and exits port B; C is the metal cathode and D is the window assembly.

can be placed inside the yoke of a permanent magnet for use with a relatively light weight field instrument or inside an electromagnet if line shape as a function of magnetic field is required. Placement in a permanent magnet is pictured in Figure 8.

The discharge is maintained by imposing two separate sources of power on the electrodes between the magnetic poles (see Figure 7). A constant current power supply capable of delivering from 5 to 300 mA at 600 volts is coupled to the electrodes through a radiofrequency (rf) blocking choke. A rf oscillator (40 MHz) that delivers 15 watts output power is coupled to the same electrodes through a rf coupling capacitor (1000 picofarads) that is rated at 600 volts. The discharge occurs in a partial vacuum obtained by bleeding argon through A (Figure 7) while evacuating through port B.

Two recent developments have greatly stabilized this discharge system. Fluctuations in light intensity were associated with two processes occurring in the discharge region: arc wander and pressure change. Arc wander caused changes in intensity reaching the detector because the focused image would move off the slit of the spectrograph. Several processes contribute to arc wander. If oxygen or water vapor are present, the electrodes may oxidize causing a region that had formerly been conductive to become relatively nonconductive. The same effect occurs if build up of sputtered material from the electrode causes a region that had formerly been nonconductive to become conductive. This tendency to wander can be greatly reduced by applying the electric field in such a manner that the attraction for ions is much stronger at one point than at any other point. Initially the discharge chamber housing was grounded and the two electrodes oppositely charged. Great improvement resulted when one electrode was shorted to the grounded housing and the other electrode was negatively charged. With this configuration, no matter where an argon ion was formed it was strongly attracted to the cathode. The sputtered material from the cathode was excited before traveling far and the spectral line emission was concentrated in a small region close to this electrode. This arrangement greatly increased the stability of the discharge and should also lessen the effects of sputtered material on the lifetime of the light source.

The pressure in the discharge region greatly affects the type of spectral emission that occurs. Whether DC or rf power is used, the process involves collisions of electrons, accelerated by an applied electric field, with gaseous atoms in the discharge chamber. The details of this process for the DC case are described in an article by G. Frances [10] and for the rf case by S.C. Brown [11]. Experimental data on the variation of line intensity with pressure from the work of L'vov [8] is presented in Figure 9. These data indicate that a change in pressure of 1 torr (133 Pa) can cause almost a factor of two change in light intensity. Such variations occur because the energy transfer from colliding electrons determines which atomic states will be populated and therefore which transitions will be involved when the atoms return to the ground state. The energy content of the electrons is determined by the voltage drop they experience before undergoing a collision. This, in turn, is determined by the gas pressure. It follows that to minimize intensity fluctuations in the discharge, the pressure

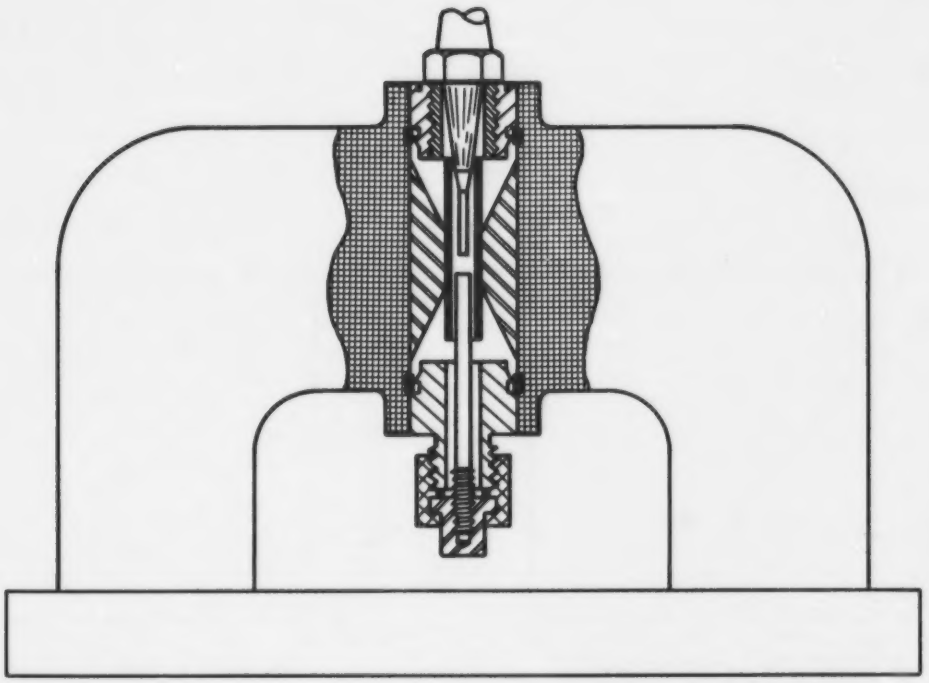

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Figure 8. Magnetically contained discharge lamp in a permanent magnet.

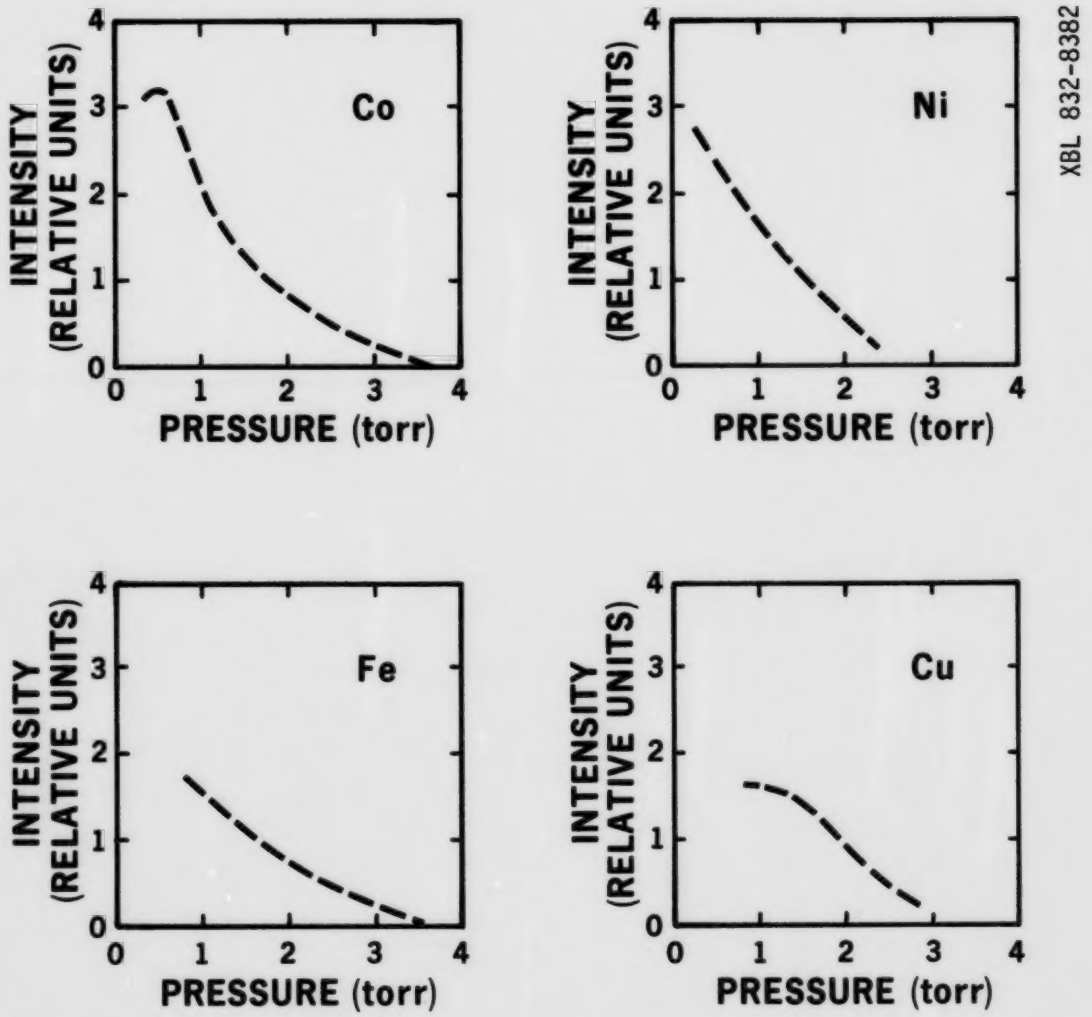

Figure 9. Relationship of lamp emission intensities to pressures of carrier gas [8].

should be held constant.

A pressure regulating system was assembled that consisted of a pressure sensing transducer (National Semiconductor Corp., Santa Clara, CA), an electrically controlled flow valve (A.M. Controls, San Carlos, CA), and the necessary electronics to cause the valve to restrict or increase flow in response to the transducer. In some cases pressure variations occurred in the discharge region because of outgassing of the electrode material. This problem was alleviated by vacuum fusion of the cathode material. In order to excite the more volatile elements, e.g. Cd, Pb, As; a boron nitride cap of the type pictured in Figure 10 was constructed. This cap slips over the metal cathode and rests on a ceramic sleeve. It seems to act somewhat like an atomic beam oven and produces a steady atomic vapor stream. The element to be excited is packed into a stainless steel cup attached to the cathode. The horizontal hole is the region of most intense discharge and its image is projected through the TALMS instrument.

A further improvement in stability of lamp operation was obtained by using a negative feedback circuit. Figure 11 is a schematic of this circuit. This device simply raises the power to the lamp driver when the photomultiplier tube (PMT) output decreases and lowers the power when the PMT output increases. The newly developed magnetically confined lamp (MCL) responds almost instantaneously to this control. The response time is approximately

$$1/8 \text{ kHz} = 8 \text{ msec}$$

The net result is a stable light output and an increase in the lifetime of the light source since the control circuit restricts the sputtering of cathode material to the amount required for constant light output. The best operating condition is determined by decreasing the input power while monitoring the PMT output on a scope. As the power is decreased, a point will be reached when the output shows the effects of shot noise. The power should be increased until this effect becomes negligible and run at that setting. The power input should not be excessive if the lamp is to last a long time.

These improvements in light source operating conditions should expand the application of the TALMS technique. If a greater number of intense atomic lines are available, a larger number of molecules can be detected. Developments thus far indicate that it may soon be possible to construct sealed off lamps that can excite either neutral atom or ion spectra at high intensity with low noise and with long lifetimes. If this is achieved, relatively light, portable instruments can be constructed for field monitoring.

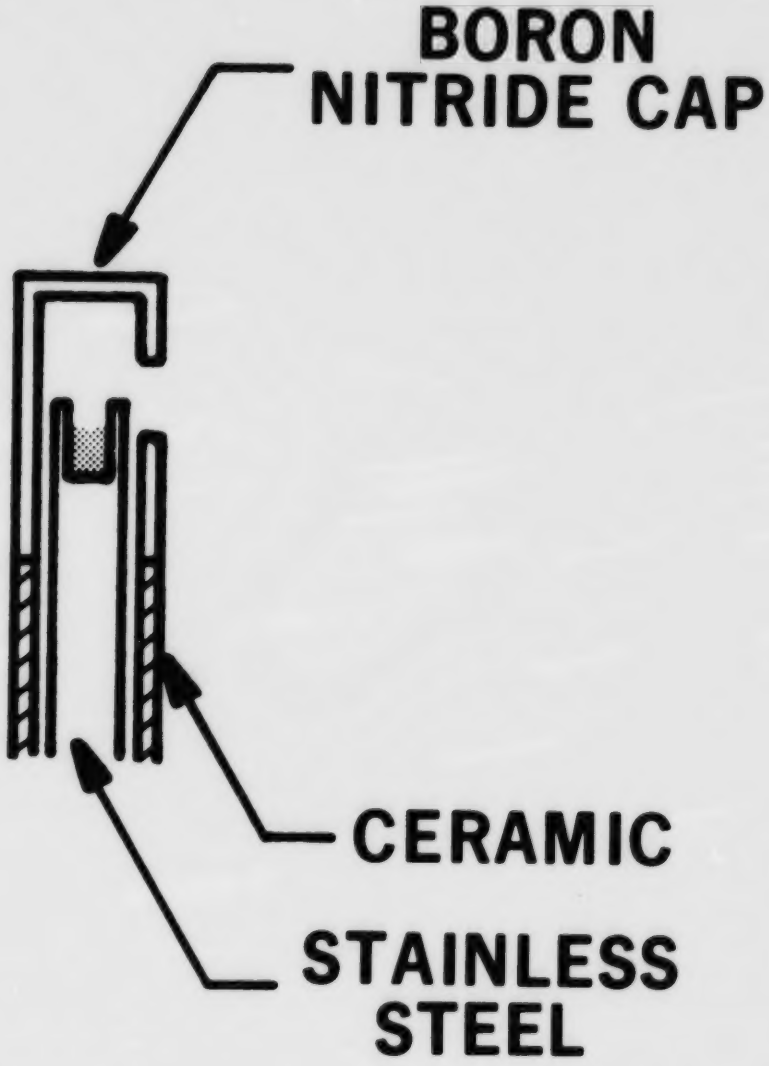

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Figure 10. Boron nitride cap for excitation of volatile elements in magnetically contained lamp.

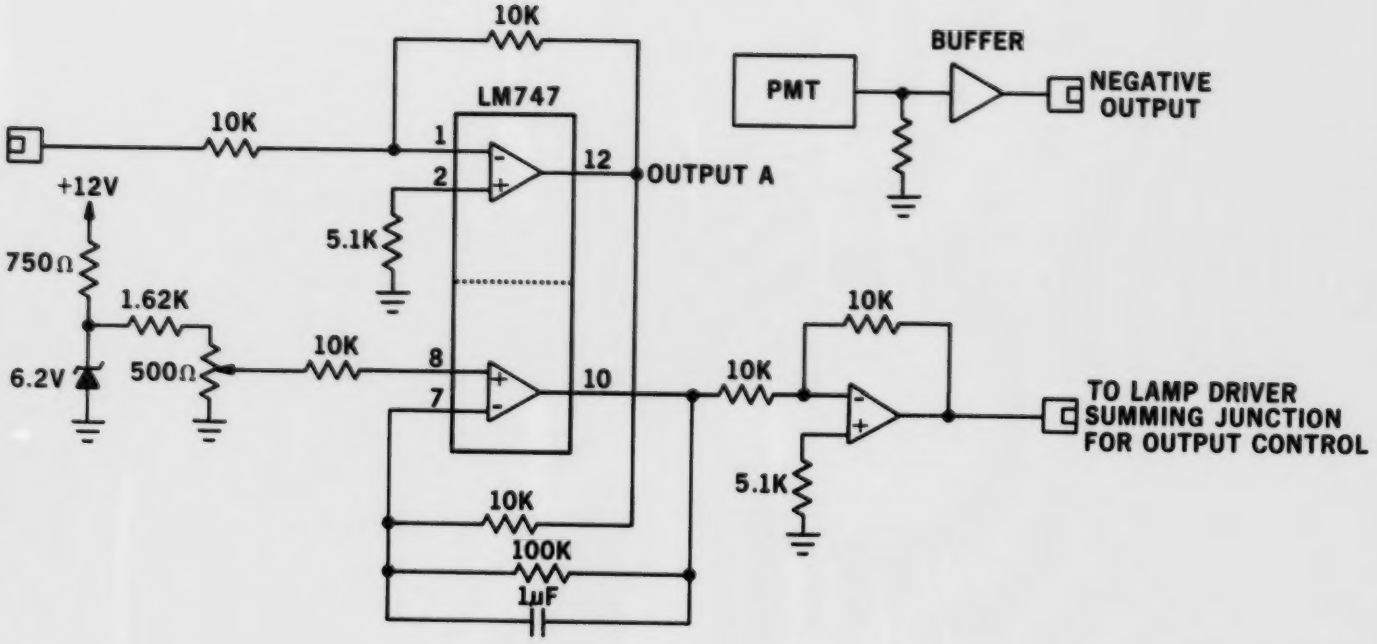

Figure 11. Negative feedback circuit for lamp stabilization.

ELECTROOPTICAL MODIFICATIONS

At the same time quiet discharge conditions for the lamp were being investigated, reduction in light source noise was also achieved by double beam operation and by use of a negative feedback circuit. The optical path for double beam operation is diagramed in Figure 12. This system will compensate for flicker noise if the AC component of the output of PMT #1 is subtracted from that of PMT #2. However, if these two signals are to track each other, the phase and time constants must be as nearly equal as possible. The gain of the two PMT's need not be equal as processing by logarithmic amplifiers renders the AC component independent of gain. In order to minimize differences in these parameters, a signal generator with DC bias was constructed to simulate a light source having the characteristic:

$$I = I_o(1 + A \cos^2 1/2\omega t)$$

where: I = the intensity after passing through the cell

I_o = intensity before passing through the cell

$\cos^2 1/2\omega t$ = the AC component caused by analyte absorption

and A is a parameter proportional to the intensity of the analyte absorption.

[I_o can vary because of broad band absorption (e.g. smoke) or because of a variation of intensity of the light source (flicker noise)].

The output of the signal generator was actually characterized by the function $V + A \cos \omega t$. This can be seen to be equivalent from the following relationships:

$$\cos^2 1/2\omega t = 1/2(1 + \cos \omega t)$$

so

$$I = I(1 + A \cos^2 1/2\omega t) = I\{1 + A(1/2 + 1/2\cos \omega t)\}$$

$$= V + A \cos \omega t$$

A variable gain was built into this equipment so the signal was finally characterized by the function $G(V + A \cos \omega t)$ where the variable gain now duplicates the behavior of the variable I_o. This signal generator was used to modify the existing signal processing electronics so that differences in gain, phase, and time constant would be minimized.

The processing electronics for the TALMS signal consists of two separate components:

1) a logarithmic amplifier that is necessary to maintain a linear relationship between the TALMS signal and the concentration of the absorbing

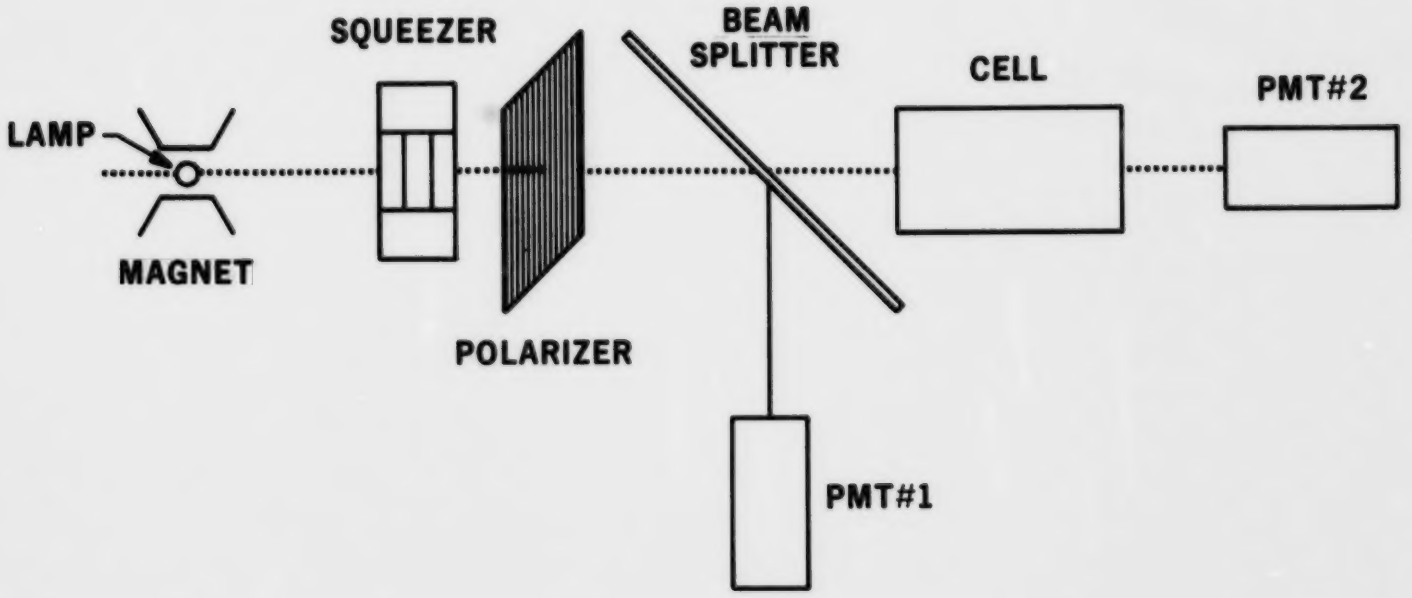

Figure 12. Optical arrangement for double beam TALMS system.

molecule and
2) a lock-in amplifier that improves the signal to noise ratio by rejecting all electrical impulses except those that have an AC frequency that is equal to the frequency of the squeezer (current controlled retardation plate).

The signal generator was used to optimize these two components for operation with the double beam arrangement.

The TALMS signal is of the form A cos ωt and must be independent of the light source intensity. Therefore the output of the first detection element (the log amplifier) must be independent of I (or G). that is, the AC component must not be changed by these components. The effect of the log amplifier is to change the signal to the form

$$\log[G(V+A \cos \omega t)]$$

Rearranging, this can be written as

$$\log GV[1 + A/V \cos \omega t)$$

which equals

$$\log GV + \log(1 + A/V \cos \omega t).$$

Therefore, at least theoretically, the AC component is independent of the gain after passing through the log amplifier.

Two log amplifiers (Analog Devices Inc. Model 755P) were placed in the same NIM module with the proper compensation networks and a supply voltage of $\pm$15 volts that originated in the $\pm$24 volt NIM connector and was controlled with a $\pm$ 15 volt regulator. Under these conditions, the two amplifiers tracked each other within 2% as specified by the manufacturer. The circuit sketched in Figure 13 was constructed, and tests were conducted to determine the effect of changing the gain. Experimentally it was found that cos ωt remained constant at G values greater than 0.01 after which the AC amplitude increased. Hence, the light may be attenuated down to 1% of the original value without appreciably affecting the measurement.

It is important to note that in order for the two log amplifiers to track each other, the DC offset in both units must be carefully adjusted. The simplest procedure is illustrated in Figure 14. Display AC (1) and AC (2) on a CRT and adjust the DC offset of one such that the amplitude remains constant as G -> 0, or as close to remaining constant as possible. Repeat this process with the second output. Then make certain that log amplifier #1 and log amplifier #2 track each other by connecting the outputs to a two pen recorder. This was done in the dual log amplifier system mode and found to track quite well for $0.05 < G < 1$ or higher.

To determine the tracking capability of the complete system, including the lock-in amplifiers, the arrangement shown in Figure 14 was used with AC

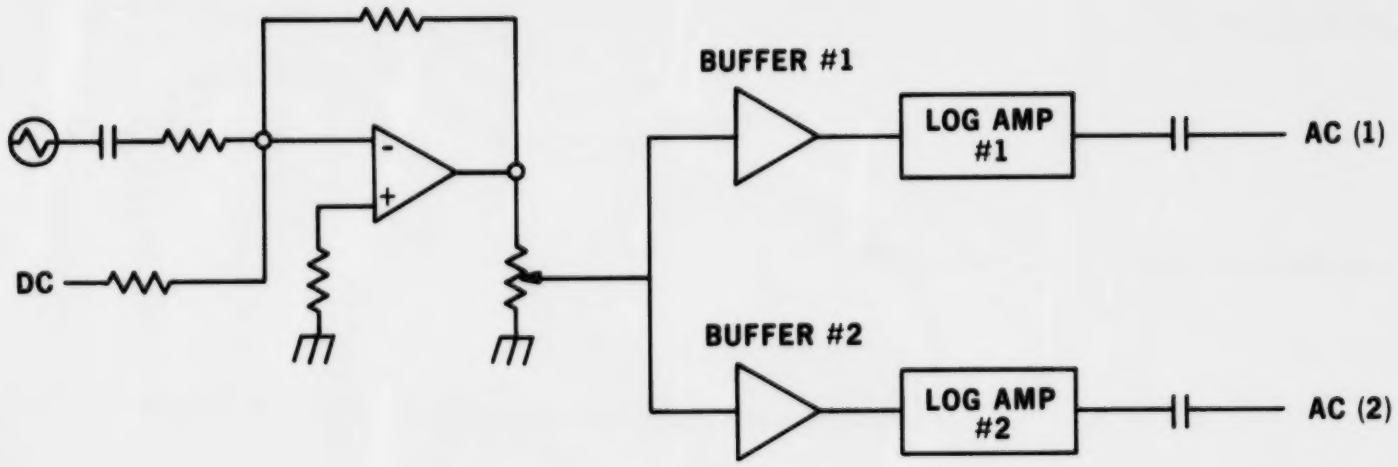

Figure 13. Circuit for testing logarithmic amplifiers.

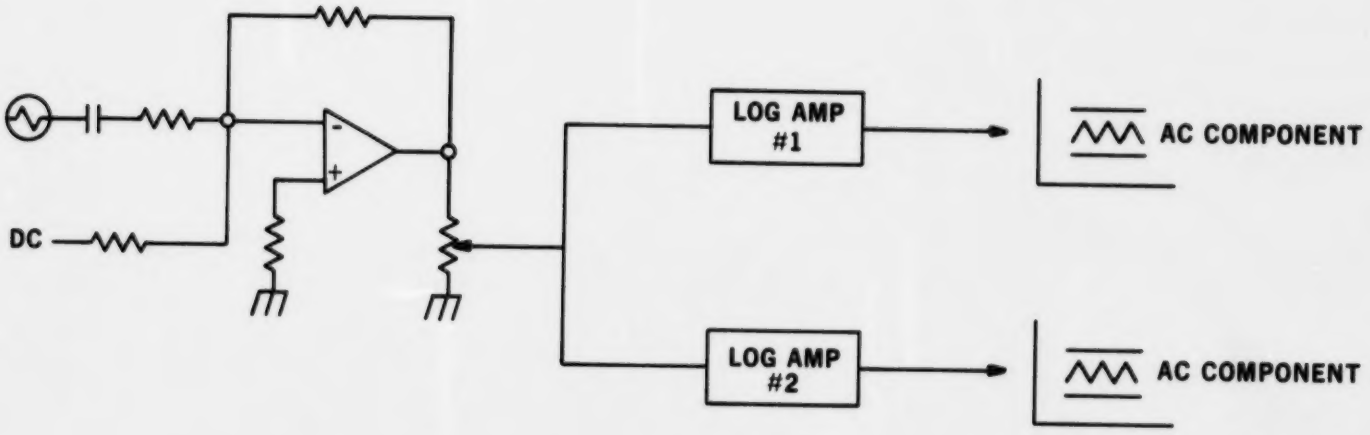

Figure 14. Circuit for adjusting logarithmic amplifiers.

(1) and AC (2) supplying the input to two AD 503K operational amplifiers that were part of the lock-in amplifier circuit. Each lock-in amplifier had already been tuned using the signal that resulted when a quartz plate was inserted at an angle to the optical axis. However, when both lock-in amplifier signals are displayed on a dual beam scope, a slight frequency difference was observed. The tuning frequencies were adjusted until the two signals overlapped. Next the gain of the lock-in amplifiers were adjusted until both signals coincided. The mixer output was monitored and again adjustments made until the displays coincided. It was found that the tracking capability was excellent after following these procedures.

The system was then tested. A difference amplifier was introduced between the lock in amplifiers and the recorder shown in Figure 15. Comparing the double beam signal with the single beam, a common mode rejection (CMR) of ca. 50 was obtained. Next a stream of air was directed at the mercury light source so that the lock-in amplifier output was decreased by one volt. The output of the difference amplifier was changed by only 1/40 of a volt. The experimental results with benzene are displayed in Figure 16. With single beam operation the detection limit of this system was 300 ppm-v. With double beam operation the detection limit was 4 ppm-v. Hence, improvement by a factor of 75 was obtained, which is consistent with the CMR indication. Another order of magnitude may be obtained by simply increasing the cell length to 60 cm.

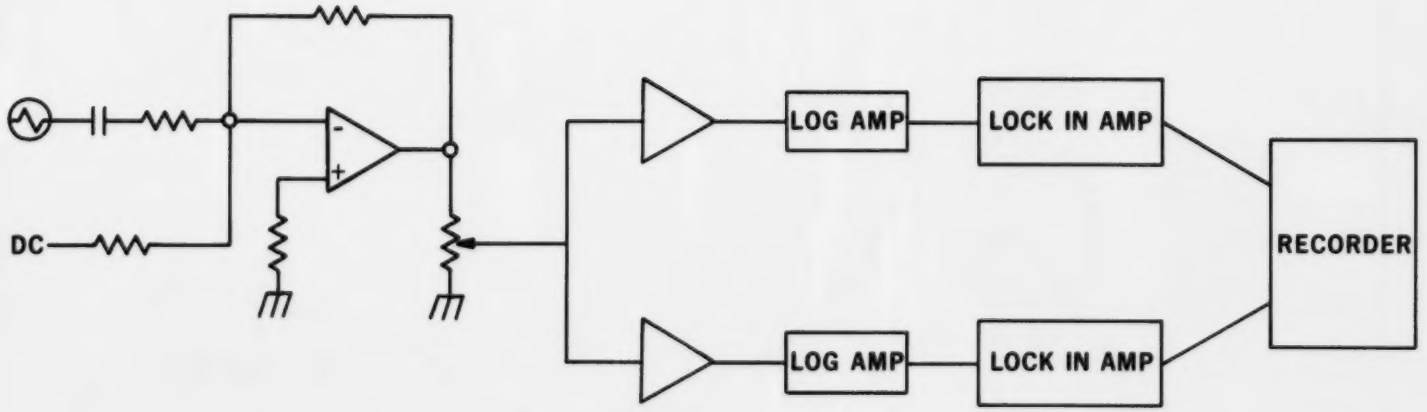

Figure 15. Circuit for adjusting lock-in amplifiers.

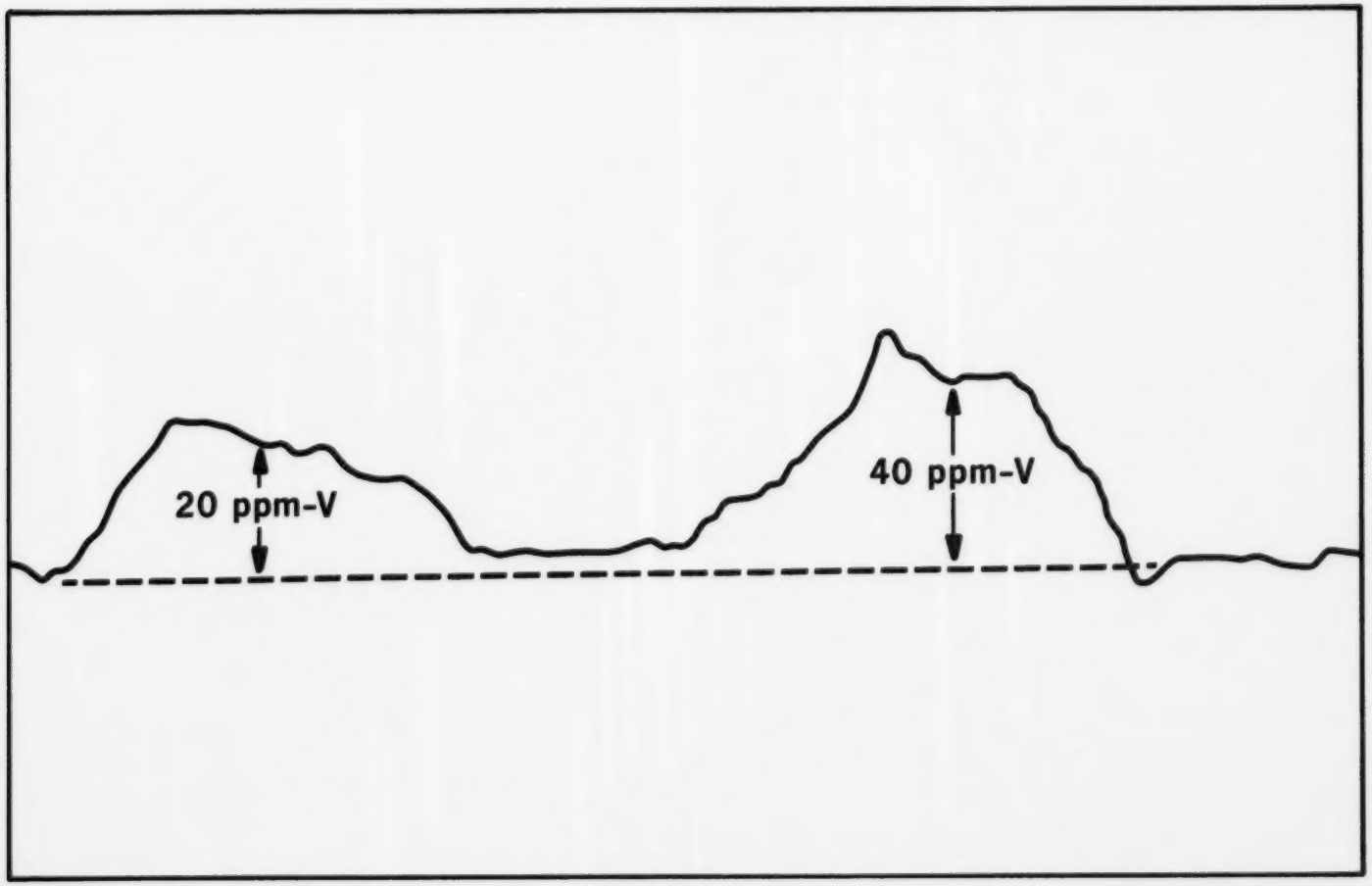

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Figure 16. Benzene signal at 253.6 nm with a double beam TALMS.

ATOMIC LINE SELECTION

Intense light sources resulting from the use of techniques just described will make available more atomic lines for matching different molecular absorption features. If more intense absorption features can be used, great improvements in detection limit may result. Also, in the event an interference occurs at one wavelength, another absorption feature may be chosen that is interference free. However, it is not possible to find matches of atomic lines with molecular absorption features entirely from searching the literature. Only limited spectral regions are usually investigated. In many cases the position of the molecular absorption will not have been determined accurately enough to choose an atomic line within one or two cm^{-1} (0.005 - 0.01 nm) of the peak. For benzene, some guidance is available in the high resolution study of Atkinson and Parmenter [12]. Also, the relative emission intensities of atomic lines are notoriously dependent upon discharge conditions. Hence, intensities listed in the literature do not have direct application to the intensities emitted by the TALMS light source. For these reasons matching should be determined by the superposition of high resolution molecular and atomic spectra [13].

Information from medium to high resolution matching experiments can also be used to predict relative TALMS sensitivities of various absorption features*. To do this a concentration independent parameter, ΔE, is defined as follows for the parallel configuration,

$$\Delta E = E^{-} - E^{+}$$

where E^{-} = the extinction coefficient of the light shifted to lower wavenumber (σ^{-} components)
and E^{+} = the extinction coefficient of light shifted to higher wavenumber (σ^{+} components).

For the perpendicular configuration,

$$\Delta E = E^{\parallel} - E^{\perp}$$

where $E^{\parallel}$ is the extinction coefficient for light polarized parallel to the magnetic field (π components)

and $E^{\perp}$ is the extinction coefficient for light polarized perpendicular to the magnetic field (σ^{-} and σ^{+} components).

The TALMS absorbance signal is equal to

$$S = \Delta E C l$$

where C = concentration in M/L and l = cell length in cm.

This technique was investigated for benzene by superimposing the emission spectra of Hg, Fe and Co upon the benzene absorption spectrum. The medium resolution absorption spectra were obtained on a Jarrell-Ash 3.4

*We wish to thank D. R. Scott of EMSL/EPA for this development.

meter spectrograph (Ebert mount) with a 600 1/mm grating used in the second order. Exposures were of the order of one minute using a 50 μm slit and a 10 mm cell. Atomic lines from a magnetically confined arc were superimposed on the absorption spectra which were recorded on Eastman SA1 plates.

A comparison of the benzene spectrum from 247 to 259 nm with the Co emission spectrum is presented in Figure 17. It will be immediately noticed that two Co lines are in near coincidence with the sharp benzene maximum at 39,534.6 cm^{-1} (vac.). The densitometer tracing shown in Figure 18, demonstrates that the Co II line is more suitable than either the Co I or a nearby Fe line for shifting onto the sharp benzene feature. The coincidence of the Hg line at 253.6 nm with the benzene feature at 39,412 cm^{-1} (vac.) had been established from earlier work [1]. Figure 19 shows the experimental absorption line shape of the benzene maximum (E = 75) which is centered near 253.6 nm along with the Zeeman pattern of the Hg line at a magnetic field of 20 kG (2.0 tesla). The extinction coefficients for the sharp benzene absorption features were obtained from the work of Atkinson and Parmenter [12] and the present study. The largest TALMS signals are obtained at the highest magnetic field. In this case the difference in extinction coefficients for the parallel TALMS configuration is

$$\Delta E = E^{-} - E^{+} = -4.9$$

while the value for the perpendicular configuration is

$$\Delta E = E^{\parallel} - E^{\perp} = 9.4$$

Therefore, one should use the perpendicular configuration to detect benzene with the Hg 253.6 nm line. However, the values of ΔE show that the TALMS signal with this feature is relatively low and a more intense band is desired for better sensitivity.

A consideration of intensities on the photographic plates and the Zeeman splitting patterns of Co and Fe lines relative to the benzene absorption profile at 252.87 nm (E max ~500) reveals that the main contribution to the TALMS signal comes from the Co II 252.86 nm line. The extinction coefficient difference for the parallel configuration with this line is approximately equal to 400. For the perpendicular configuration it is about - 100. Therefore, the parallel configuration should give a better TALMS signal.

We shall next compare the experimental TALMS signals that result from the perpendicular configuration for the Hg I and Co II lines. Figure 20 shows the absorption of the perpendicular and parallel polarized components of the Co II line at a magnetic field of 27 kG (2.7 tesla) by benzene vapor. There is almost no absorption of the parallel (π) components while ~50% of the intensity of the perpendicular (σ) components is absorbed. This is due to the fact that one set of σ components overlap the benzene absorption band while the other set are outside the region of benzene absorption.

As shown in Figure 19, when the TALMS signal is obtained using the Hg 253.6 nm line, the parallel components are more absorbed by the vapor than

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Figure 17. Tracings of photographic plates of benzene absorption:

Upper: Benzene absorption.
Lower: Co emission spectrum.

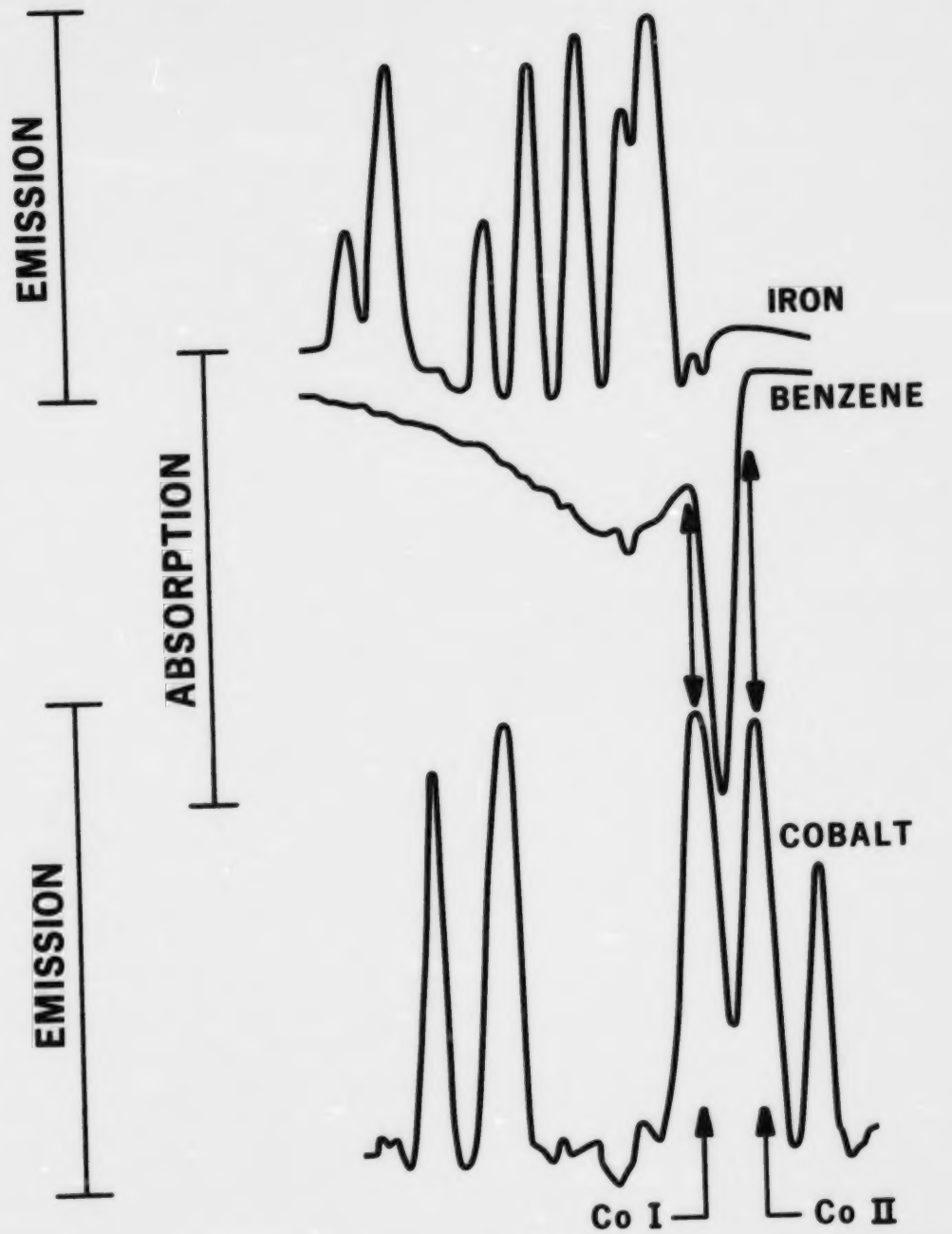

Figure 18. Medium resolution benzene absorption spectrum and emission spectra of Co and Fe in the region of 252-253 nm.

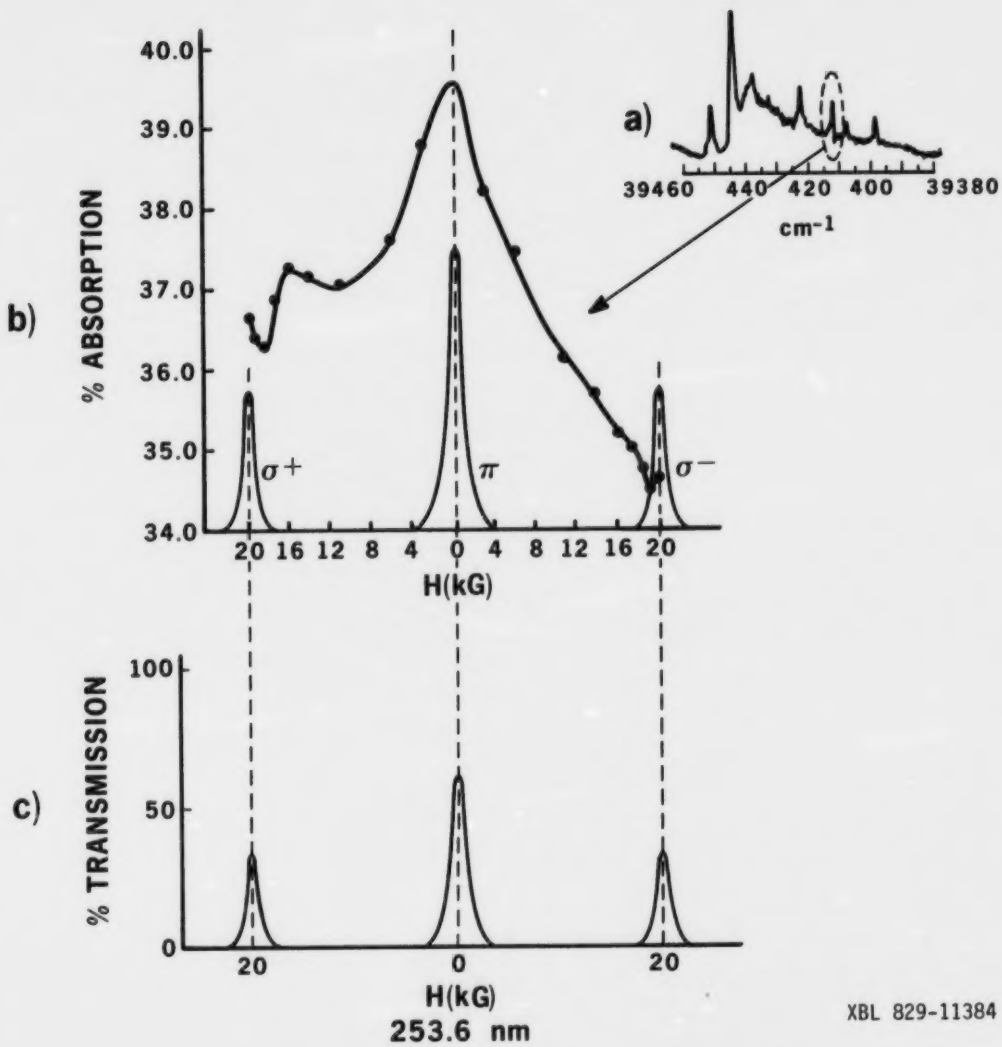

Figure 19. High resolution absorption spectrum of benzene and Zeeman split Hg 253.6 nm line:

a) Absorption spectrum [12].
b) Zeeman scan (using isolated σ^+ and σ^- components) and Hg Zeeman pattern of region dotted in (a).
c) Zeeman components transmitted by benzene at 2.0 T (20 kG).

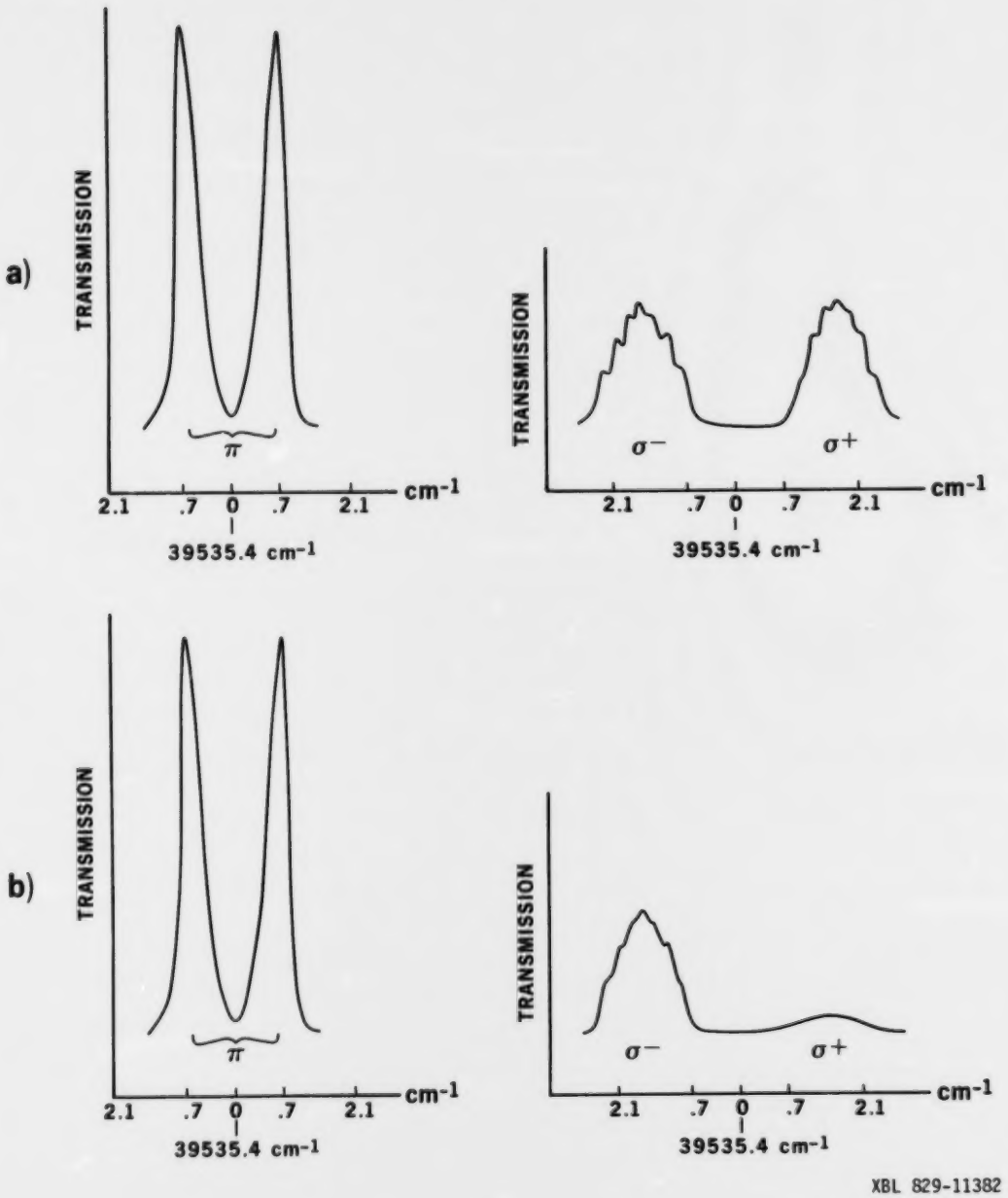

Figure 20. Absorption of the Co II Zeeman components at 252.9 nm by benzene.

a) Before absorption
b) After absorption

are the perpendicular components. This is completely opposite from the Co II case, i.e. the TALMS signals are 180 degrees out of phase. Figure 21 illustrates the periodic change in the light intensity as the phase-squeezer-polarizer unit switches from detection of parallel to perpendicularly polarized light. The peak to peak amplitude represents the differential absorption signal that corresponds to the TALMS signal. This amplitude is proportional to the quantity of benzene in the light path. It is quite clear that a phase difference of 180 degrees exists between the signal from the Co II line and the Hg I line.

The strength of the TALMS signal in the perpendicular configuration is directly proportional to the extinction coefficient difference. For the Hg 253.6 nm line the signal, S, is given by

$$S = 8.4\ C1$$

while for the Co II line it is

$$S = 100\ C1.$$

Therefore the Co II signal should be 12 times the Hg I signal.

Figure 22 shows the experimental TALMS results. These data indicate the TALMS signal for the Co II line is 35 times that of the Hg I line. The disagreement of the estimated and experimental signals is due to difficulties in determining absolute absorbances from photographic plates and the contribution of the Co I Zeeman components to the experimental signal. The Co I line was not taken into account in obtaining the estimated value.

This work demonstrates that the use of high to medium resolution absorption spectroscopy with superimposed atomic lines is an efficient method for locating near coincidences between atomic lines and sharp molecular absorption features. Also the difference in extinction coefficient is shown to be the important parameter in determining the magnitude of the TALMS signal.

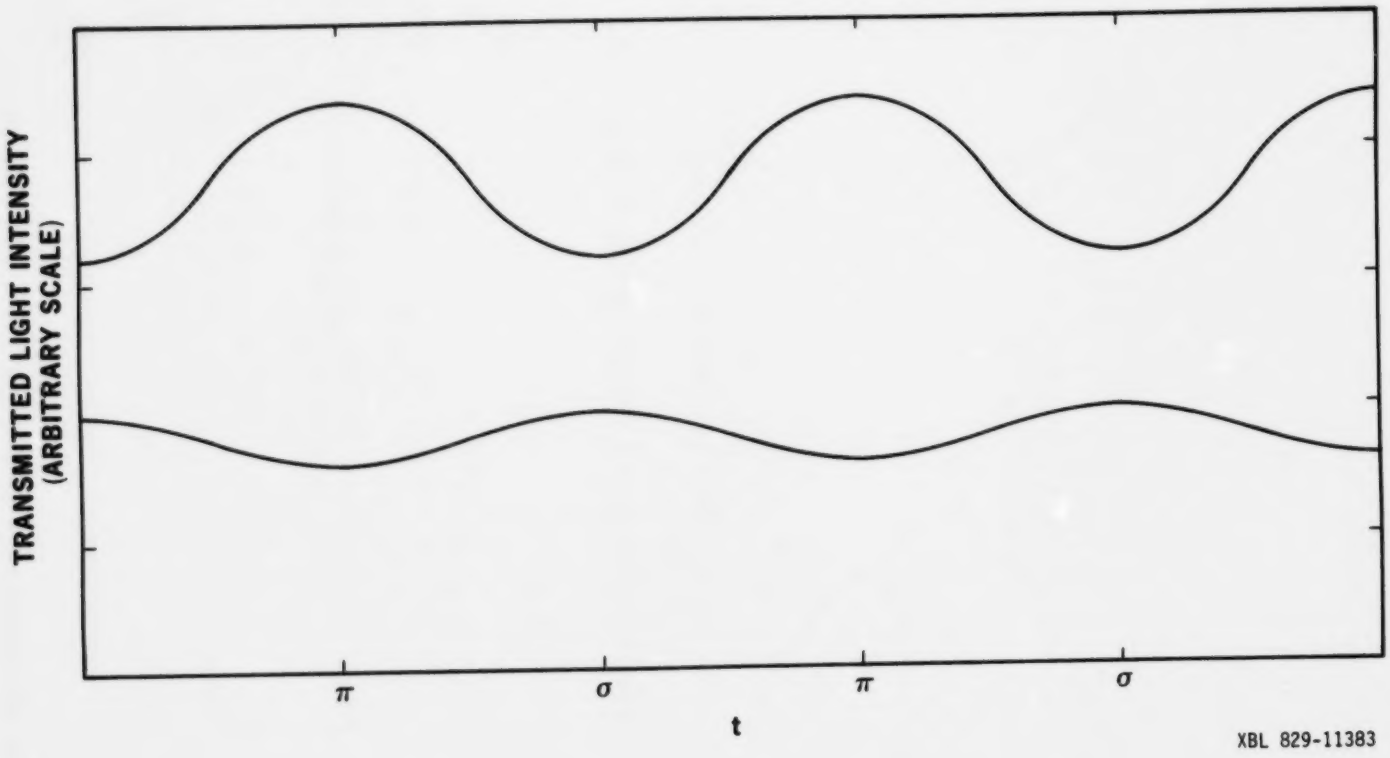

Figure 21. TALMS phase differences for benzene.

Upper: 252.9 nm Co II signal at 2.7 T (27 kG).
Lower: 253.6 nm Hg signal at 2.0 T (20 kG).

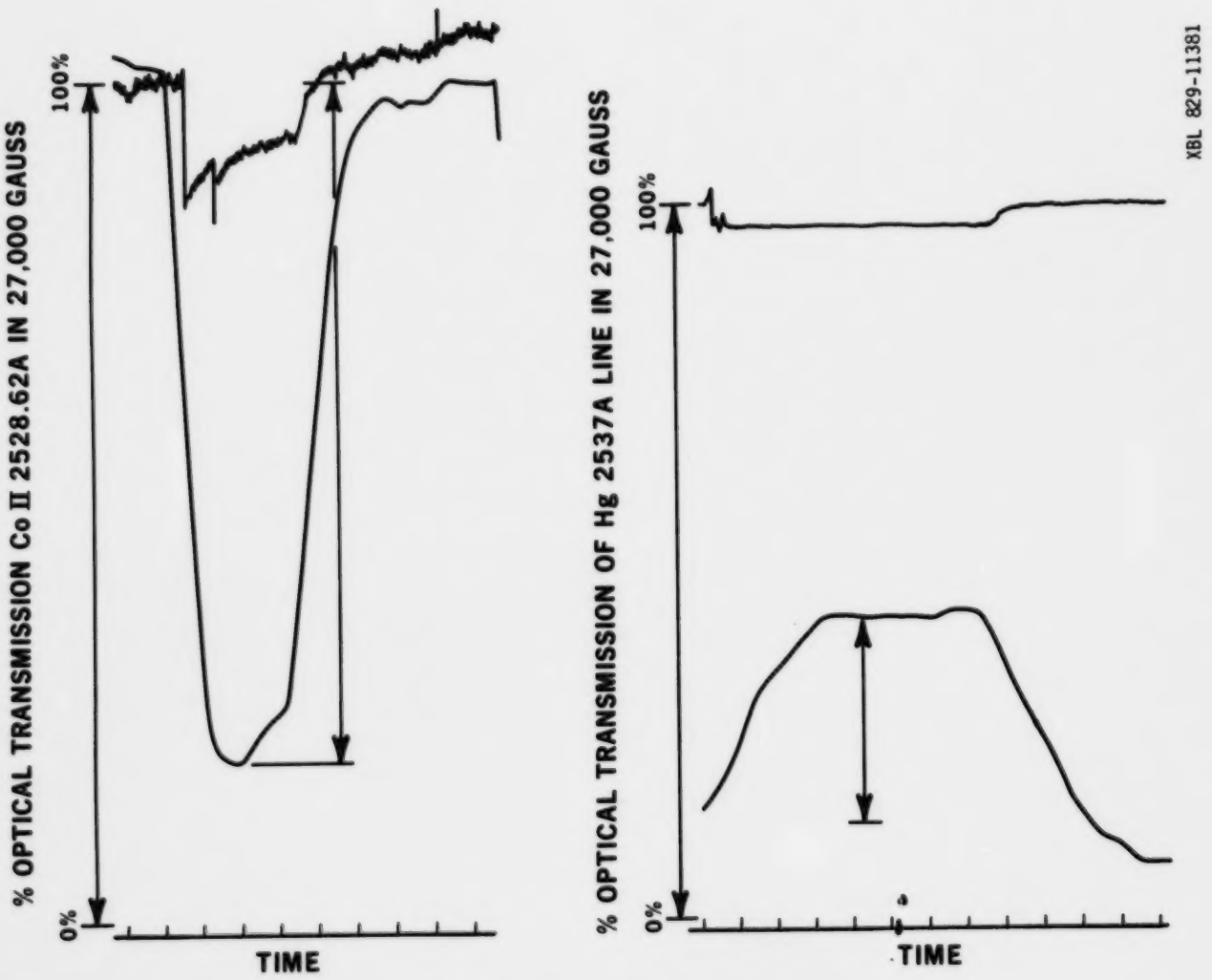

Figure 22. Benzene TALMS signals with Co II and Hg lines.

Left: Co II 252.9 nm line at 2.7 T (27 kG) with 78 ppm-v benzene and gain = 1.
Right: Hg 253.6 nm line at 2.0 T (20 kG) with 78 ppm-v benzene and gain = 10.
The upper curves are the optical transmission and the lower curves are the TALMS signals.

TEMPERATURE AND PRESSURE EFFECTS

Instrument performance can be influenced by the temperature and pressure inside the absorption cell because of line broadening and shifting. In fact, if molecular features can be shifted by controlling these parameters, it might be possible to achieve better matching of atomic lines and molecular absorption features and thus improve the detection limit. The effect of temperature on an single band is easy to predict if Doppler broadening dominates. The molecular line width is determined by Doppler broadening according to the expression:

$$W = C\sqrt{\frac{T}{M}}$$

where W = the line width
T = the absolute temperature
M = the molecular weight
and C = a constant

Hence, the expected effect of increasing the temperature is to increase the line width. For example, an increase of temperature from room temperature (293 ^{o}K) to 100 ^{o}C (373 ^{o}K) would increase the line width about 12 %. However, it is not clear that Doppler broadening is the dominant factor in molecular line widths since overlapping rotational lines are the underlying cause of the sharp features. A change in temperature can alter the population of low energy rotational levels so that the intensities of the rotational transitions will change. This effect could alter the shape of the sharp features. Scott and Hedgecoke (U.S. Environmental Protection Agency, Research Triangle Park, North Carolina) have found temperature effects of the benzene TALMS signal at 253.6 nm. However, as yet, this work has not been duplicated at the Lawrence Berkeley Laboratory.

Pressure effects on the TALMS signal are not well understood. Experimental pressure effects on the spectrum of aromatic compounds have been reported by B. Vodar [14]. A red shift is observed that is proportional to pressure when gases such as nitrogen, argon, hydrogen, carbon monoxide, and carbon dioxide are used to pressurize aromatic compounds. The magnitude of shift for the phenol, nitrogen system is displayed in Figure 23. However, the application of pressure should cause broadening as well as shifting of absorption features. The TALMS signal would be expected to become weaker as absorption features are broadened. Such a decrease was observed for benzene and is described in Section 5, Analytical Tests.

Phenol was studied to determine the effects of pressure on the TALMS signal. Phenol is an important molecule to detect because it is a byproduct of petroleum refining and coal conversion technologies. and it is produced in fairly high quantities in the United States [15] There are several references in the literature describing the high resolution spectra of phenol

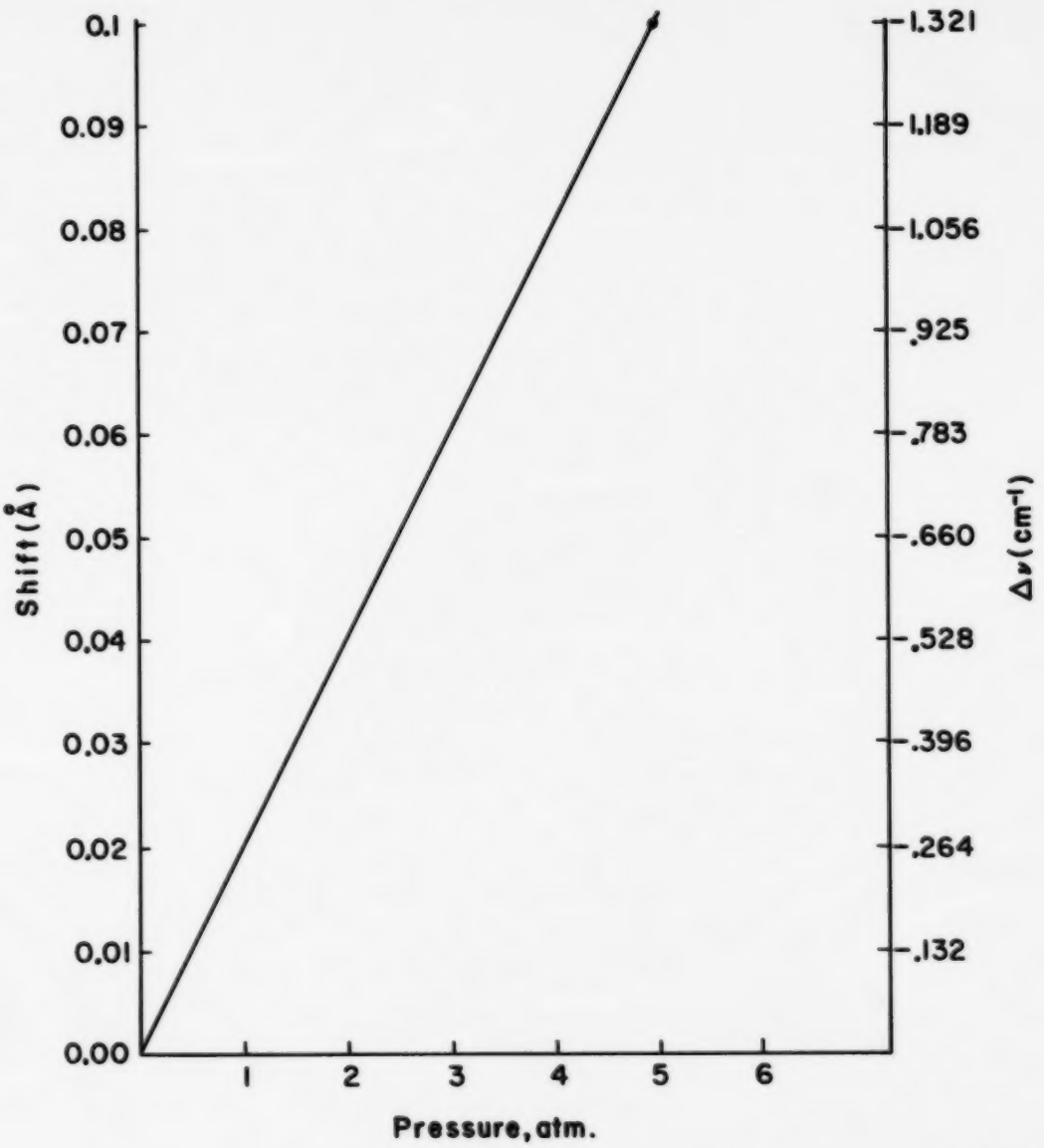

Figure 23. Pressure shift of phenol absorption near 275.0 nm [14].

[16]*. A comparison of the sharp absorption features reported in these publications with the atomic emission listed for iron in the MIT Table, indicated a near coincidence existed with the Fe 275.0 nm line. A lamp emitting this line was constructed using techniques already described. The lamp was placed between the poles of an electromagnet that delivered a field of 2.5 tesla (25 kG). Vapor in equilibrium with phenol at room temperature was injected into the cell. A TALMS signal was obtained.

Figure 24 shows the relative positions of the Zeeman split Fe I line (275.01 nm) and the sharp phenol absorption feature near 275.0 nm. In this case the perpendicular Zeeman configuration was used so positions of both the π and σ components are indicated. The phenol absorption was obtained in a cell that was first evacuated and then filled with vapor such that the pressure was 0.29 torr (3.8×10^{-4} atm). As indicated in Figure 23, a shift of ~ 1.1 cm^{-1} would be expected if the pressure were increased to 4 atm. This would cause a shift in the high wavenumber phenol peak so that it would overlap the high wavenumber σ components of the Fe line. The low wavenumber phenol peak would, at the same time, be shifted to overlap some of the π components. Pressure broadening would also be expected to affect the TALMS signal. All of these factors makes it hard to predict the final effect of raising the pressure to 4 atm. In fact, no change in TALMS signal was recorded.

This is a welcome result because for higher sensitivity it might be desirable to cryogenically trap phenol from a large volume of air. If the contents of such a trap were introduced into the absorption cell, high pressure might result because of the water also retained in the trap. (It is assumed that the temperature of the cell would be increased so that the contents of the trap would be in the vapor state). The fact that no change in TALMS signal was recorded demonstrates that corrections will be unnecessary in the event that phenol is monitored at pressures below 4 atmospheres.

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*D. R. Scott of EMSL/Research Triangle Park, NC, alerted us to these references.

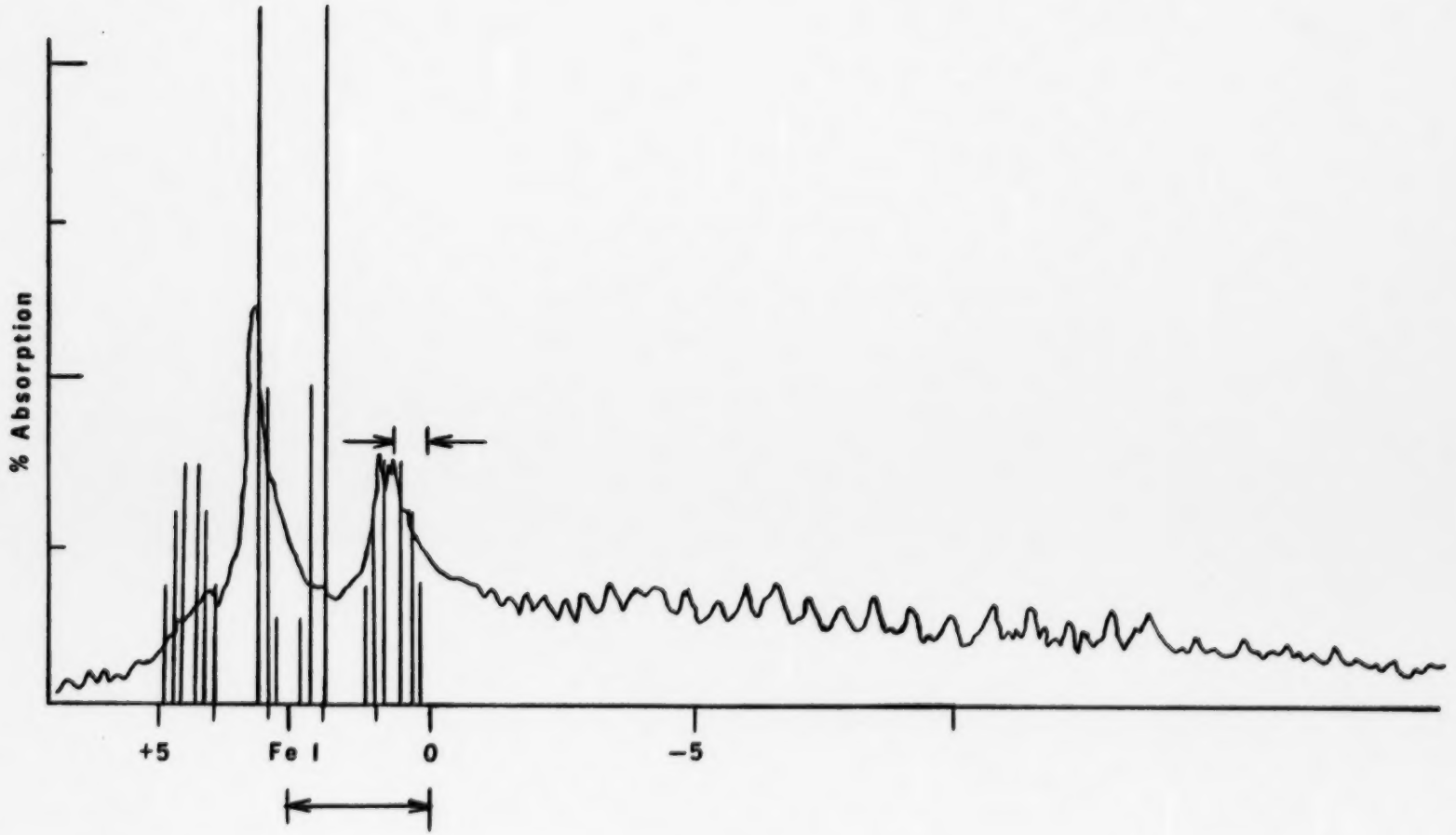


Figure 24. Absorption spectrum of phenol with superimposed Fe 275.0 nm line. Arrows indicate displacement from 0-0 transition of an intense phenol absorption and of the non Zeeman split Fe I line.

CRYOGENIC TRAPPING

In order to measure very low concentrations (e.g. ppt to ppb-v) of organics in air samples, some form of concentration is necessary. Descriptions have recently appeared of two different concentration strategies. In one case Eiceman and Karasek [17] tested the following absorbent materials:

Tenax-GC	Chromosorb 101
Florisil	Carbopack C HT

for retention of chlorinated hydrocarbons. Tenax-GC was found to be the best of the materials tested.

In the other case, R.D. Cox et al. [18] used cryogenic trapping to determine nonmethane hydrocarbons in ambient air. These workers found water trapped with the hydrocarbons did not cause problems and that results were independent of flow rate between 20 and 200 ml/min. Because this seemed like a more controllable method (there are recovery problems with Tenax-GC), cryogenic trapping was used for benzene determinations.

The trapping system is displayed in Figure 25. After preliminary testing using argon to carry benzene through the trapping system, a peristaltic pump was incorporated so that ambient air could be used as the carrier gas. This pump was located downstream from the trap to minimize pump contamination of the gas stream. A rotameter located upstream indicated flow rates of ca. 18 l/min were possible with this arrangement.

The testing procedure consisted of injecting a gaseous air-benzene mixture, obtained from a flask that contained benzene at 0 ^{o}C, into the air stream before it passed through the trap. The injection was carried out by a syringe pump whose injection rate could be varied from 0.058 µl/min to 140 ml/min. By proper adjustment of flow and injection rates gaseous mixtures ranging from greater than 1000 ppm-v to less then 1 ppb-v could be generated. After the selected sampling time had passed, the signal was obtained by closing the valves on either side of the trap, heating the trap to room temperature, and pushing the released gases through the cell at a rate of 0.7 l/min. Losses were determined by comparing the area under the signal with that obtained by rapid injection of 5 ml of the benzene air mixture into the system while the carrier gas was flowing at 0.7 l/min.

When dry ice-acetone cooling baths were used, it was found that losses would occur because the trap became too warm at the higher flow rates. If liquid nitrogen was used as a coolant and nitrogen as a carrier gas, the losses no longer occurred. However, if liquid nitrogen was used with air as the carrier gas, the trap filled up with liquid oxygen which presented a real danger when the trap was allowed to warm up with the valves closed.

These problems were solved by using the equipment pictured in the figure. The trapping period was not started until the thermocouple inside the trap indicated the temperature was less then -80 ^{o}C. The rotameter upstream from the trap was used to indicate if oxygen was being condensed in the trap. If the trap is cold enough to condense oxygen, the flow rate will

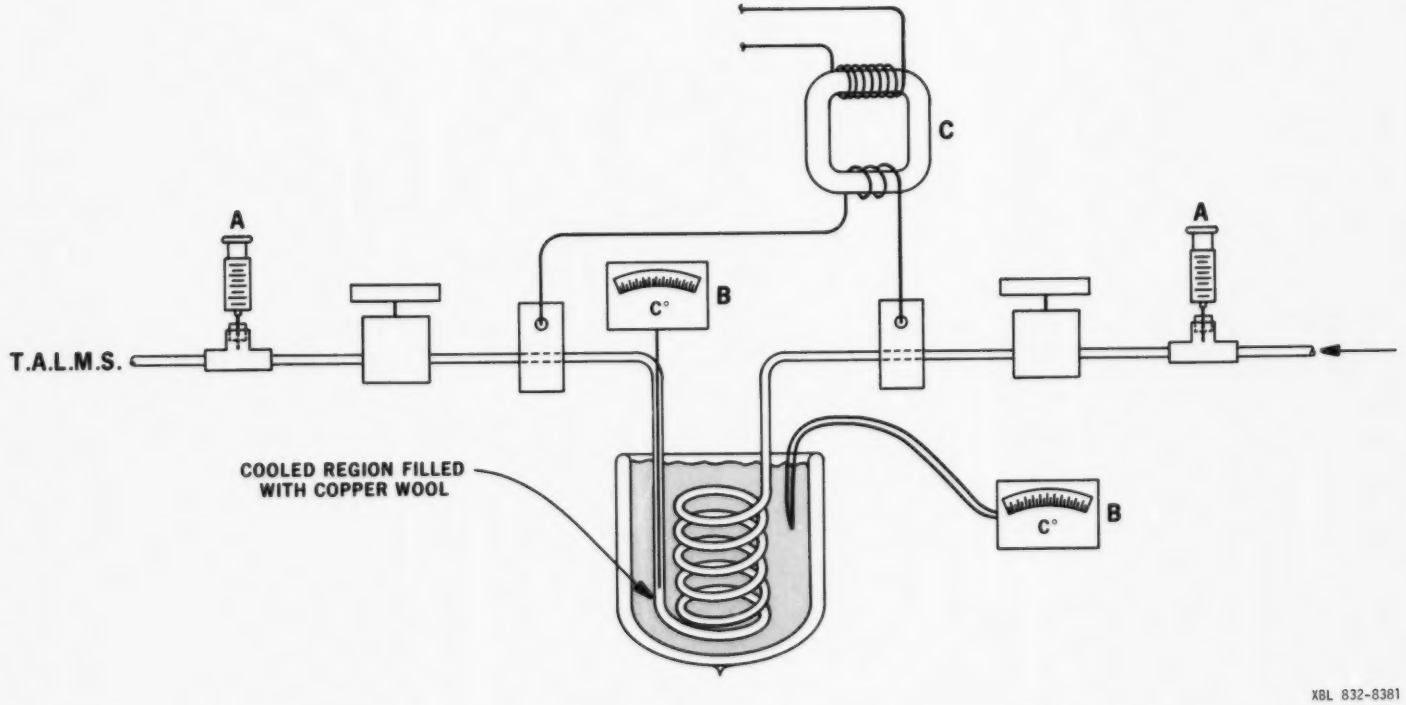


Figure 25. Cryogenic concentrator for the TALMS system; A - ports for introducing calibration gasses, B - thermocouples, C - transformer

increase dramatically. As liquid nitrogen is slowly poured in, the flow rate is monitored. If the flow rate starts to increase, the trap is heated resistively by the circuit shown in the figure. Eventually, an equilibrium situation is reached where the temperature is below -80 ^{o}C and the flow rate is unchanged from what it was when the trap was warm. When this occurs, sampling is initiated.

Following this procedure a flow rate of 18.5 l/min was used while the air-benzene mixture was injected at the rate of 0.075 ml/hr. After 50 minutes the trap plugged up such that the run had to be terminated. During this time 3.8 ml of the benzene mixture and 925 liters of air had passed through the trap. The amount of benzene that flowed into the trap is the same as if an air stream containing 130 ppb-v had been sampled. Since the signal to noise ratio was ca. four, this corresponds to a detection limit of ca. 30 ppb-v.

Sample loss was checked by recording the signal resulting when 3.8 ml of the benzene-air mixture was rapidly injected into the system and calculating the area under the curves. The value for the 50 min run was 1076 mv-sec; the values for the two rapid injections were 1116 and 1030 mv-sec. Although these results are preliminary, they indicate that no losses resulted from the trapping procedure and the precision is of the order of 5 %. They also indicate if sensitivities lower than 30 ppb-v are required interferences from water vapor must be considered.

The work just described was carried out before improvements in light source operation, that were discussed earlier, were introduced. As already indicated, the modified light source with associated electrooptical improvements has achieved a gain of 100 in detection limit. Hence, cryogenic trapping, in combination with the modified system is expected to reach a detection limit of 0.3 ppb-v.

SECTION 4

DESIGN AND CONSTRUCTION OF INSTRUMENT

The TALMS instrument delivered to EMSL/RTP as part of the FY82 IAG (IAG-AD-89-F-2A008) is pictured in Figures 26 and 27. This instrument is designed to monitor benzene although it could be easily adapted to monitor other compounds as well. The optical components are mounted on a track attached to a black base. The electronic components are contained in a sliding drawer in this base and in a NIM-Bin rack located under the instrument in these figures. Circuit diagrams are in Appendix B.

OPTICAL COMPONENTS

The optical elements as viewed from left to right in Figure 26 are:

a. The permanent magnet containing a Varian fitting that houses a mercury light source and a collimator containing a 50 mm focal length fused quartz lens.

b. A polarization compensation plate that consists of a fused quartz plate which may be rotated about an axis perpendicular to the optic axis. This device is used to change the relative intensities of plane polarized and perpendicularly polarized light emitted by atoms in the light source.

c. The variable phase retardation plate, usually called the squeezer,that changes the polarization direction of light emitted by atoms in the light source at a frequency of ca. 100 Hz.

d. A Varian tee section on which is mounted a collimator containing another 50 mm focal length lens and a linear polarizer. The orientation of the polarizer can be adjusted with a shaft that projects through a slot cut in the collimator and held in position with a set screw.

e. The Varian tee section contains a partially aluminized quartz plate that transmits part of the oncoming light through the cell and reflects part to a photomultiplier tube for double beam operation. The angle of reflection, and hence the amount of light reflected, may be varied by rotating the grey knob sticking up from this section.

f. A straight section with a 100 mm focal length lens followed by two quartz windows spaced 6.4 inches apart. The region between these windows contains the sample and encloses a volume of 134.1 cubic centimeters. This section is terminated by a second photomultiplier tube.

g. The valves for evacuating the sample cell and introducing sample into the system project above and below the straight section just described. (They can be better seen in Figure 27.) The sample introduction system also includes ports that accept septa when syringe injection is required.

These components were obtained from the following manufacturers:

a. Magnet - Permag Central Corp. Elk Grove Village, IL

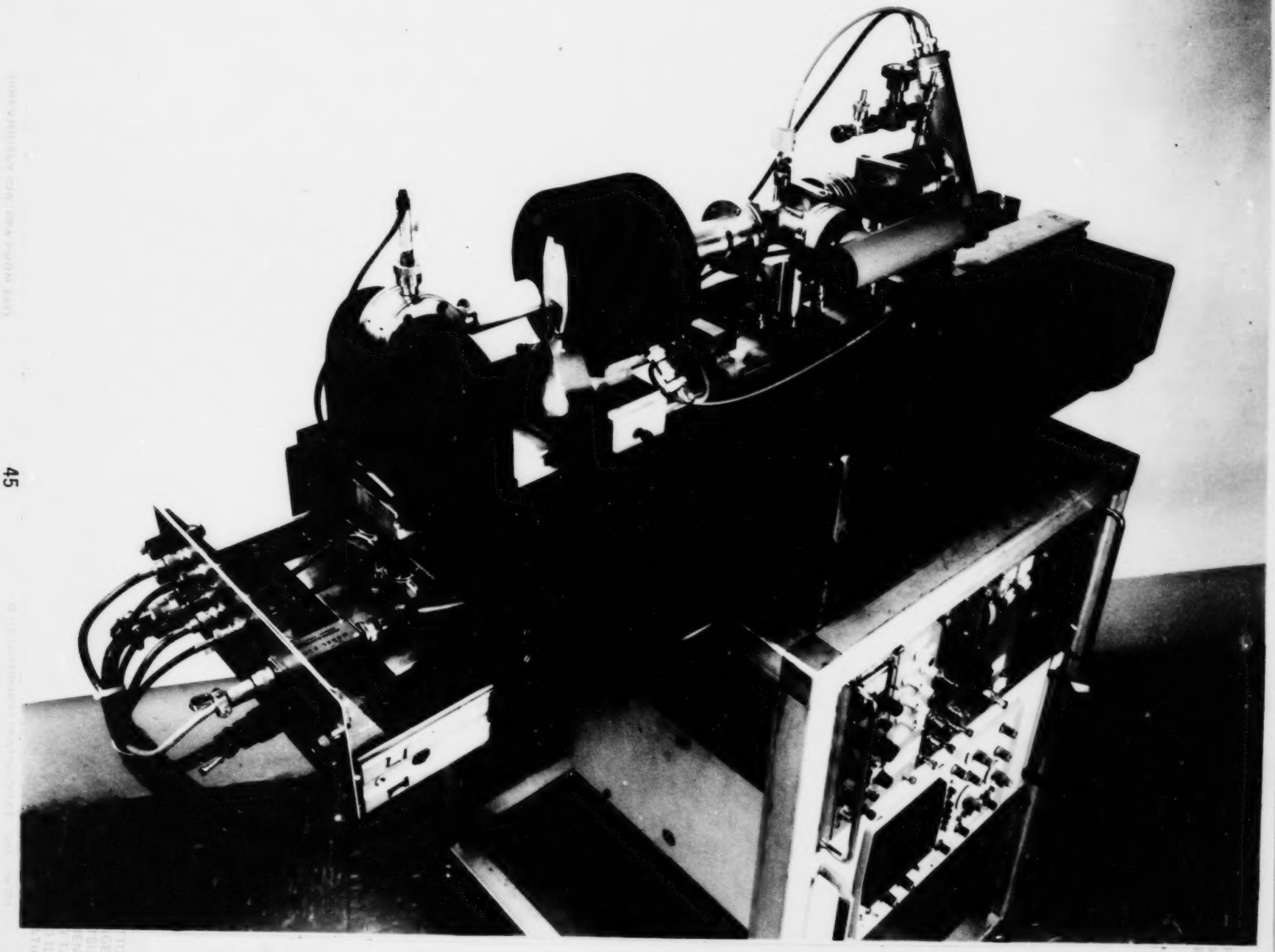


Figure 26. Photograph of TALMS benzene monitor (magnet end).

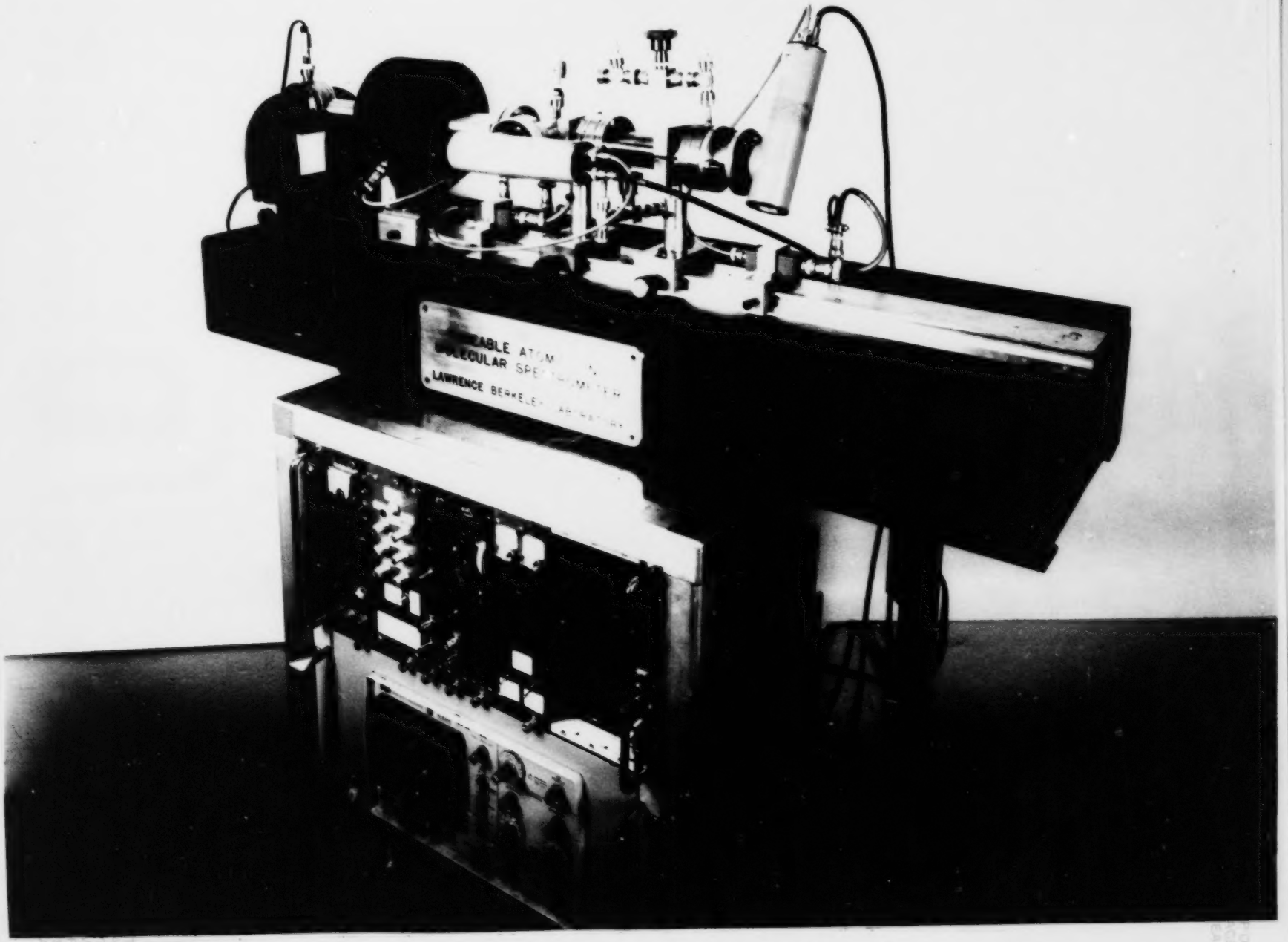


Figure 27. Photograph of TALMS benzene monitor (photomultiplier end).

b. Squeezer - fabricated at Lawrence Berkeley Laboratory

c. Lenses - Oriel Corp., Stamford, CN

d. Quartz Plates - Amersil Inc., Hillside, NJ

e. Aluminized Coating - Lawrence Berkeley Laboratory

f. Valves - Nupro Co., Willoughby, OH (bellows valves SS-4H)

g. Fittings for cell and tee section - Varian Associates, Palo Alto, CA

ELECTRONIC COMPONENTS

The power supplies and power amplifiers for the instrument are contained inside the base. The remaining electronics are housed in modules that fit into a NIM Bin rack. (The NIM Bin rack is a housing that contains electronic plug-in units so that hand built modules can be easily inserted for testing or use.) However, a NIM Bin power supply is not necessary because the elements contained in the base produce the required power.

The electronic components in the base can be removed by disconnecting the appropriate cables and sliding out a drawer that fits into the base. This drawer, and its contents, are displayed in Figure 28. They mainly consist of power supplies and power amplifiers for the squeezer and the light source. A power supply for the modules in the NIM Bin rack is also included. The approximate power requirements are: squeezer - 90 W, lamp - 30 W, NIM Bin components - 2 W. These units are designed for 120 v AC, 60 Hz power.

There are six modules housed in the NIM Bin rack. The circuit digrams for these modules are located in the appendix as part of the instruction manual.

a. The photomultiplier tube module supplies high voltage (400-1100 v) to both photomultiplier tubes.

b. The squeezer module contains an audio frequency generator that determines the rate of switching of the two polarized beams and provides the reference signal for the lock-in amplifier. This module also contains controls for varying the intensity of both the ac power and dc power supplied to the squeezer.

c. The light driver module supplies the high frequency driving signal to the power amplifier in the base of the TALMS monitor. Both the frequency and the power level supplied to the lamp can be varied with controls on this module.

d. The dual beam tracking module accepts the output from the two photomultipliers. Each signal is processed by a logarithmic amplifier and the difference is obtained using a difference amplifier.

e. The lock-in amplifier module uses phase locked detection to extract the squeezer modulated signal from the photomultiplier tubes and provides a dc output proportional to the analyte concentration in the sample cell.

f. The time constant module allows the TALMS signal to be averaged over time intervals of 1, 10, 30, 50, or 100 seconds.

In order to test instrument performance the TALMS signal was displayed on a

Figure 28. Photograph of TALMS benzene monitor electronics drawer.

chart recorder. However, this signal can also be stored and processed by the HP-85 computer using programs developed at this laboratory.

SECTION 5

ANALYTICAL TESTS

A great deal about instrument performance can be learned from the determination of the analytical curve (instrument response as a function of known amounts of analyte). This same information also serves to calibrate the instrument. Calibration for TALMS is usually accomplished by injecting a known amount of a gaseous compound into the absorption cell of the instrument. Literature values of vapor pressure as a function of temperature are used to determine the amount introduced. Corrections are made for differences in temperature and volume of the organic vapor before and after injection (temperature corrections are usually not important for benzene) . This approach allows the precision of the instrument to be tested although the accuracy remains unknown. The uncertainity in accuracy results because of possible errors in the literature values of the vapor pressure. The cell temperature is chosen to insure the compound does not exist as a polymer or a hydrate (especially important for formaldehyde). The data obtained from injections of several different amounts are plotted as the analytical curve.

This section includes descriptions of three benzene calibration procedures: benzene without preconcentration; benzene with preconcentration; and benzene field calibration. Calibration procedures for phenol and formaldehyde are also mentioned.

BENZENE CALIBRATION

Calibration when preconcentration is not required is carried out as follows:

(1) Benzene is placed in a flask fitted with a septum;

(2) The flask is immersed in an ice bath overnight;

(3) Since the vapor pressure of benzene in equilibrium with the solid at 0 ^{o}C is known, the quantity in a specified amount of air withdrawn from this flask can be calculated;

(4) Known amounts of the air, benzene mixture are withdrawn with a gas tight syringe and injected into the cell of the instrument.

Benzene may exist as a solid or supercooled liquid at 0 ^{o}C. Vapor pressure data for the solid, and not the liquid, should be used. The vapor is withdrawn from the flask by use of a syringe containing air at room temperature whose volume equals that of the gas to be removed. The needle of the syringe is inserted through the septum. The syringe is then pumped several times to mix the air with the vapor and the desired volume is removed. This is done to prevent a partial vacuum in the flask from disturbing the setting on the syringe as it is withdrawn. However, this means the temperature of the vapor is unknown. No correction for the temperature of the vapor was made, i.e. it was assumed to be at room temperature. At most, this assumption would cause a 5% error.

Data that result from this procedure are plotted in Figure 29. Each data point was obtained from a chart recorder with the instrument set to have a 10 sec time constant. The detection limit of this double beam system was found to be 3 ppm-v. A straight line relationship was found to exist over almost three orders of magnitude. The lack of scatter in these points indicates precision errors from this method of calibration are minor.

Another method of injecting known amounts of benzene is used to verify the performance of the trapping system. In this case, nitrogen or argon carrier gas is passed through the concentrating trap at a known and controlled rate. Using a variable speed syringe pump, a benzene-air mixture is slowly injected so that the gas stream contains the desired amount of benzene. After the proper amount of gas has passed through the trapping system the cell is evacuated, the trap is heated and the trap-cell system is opened to atmosphere. The incoming air serves to evenly distribute the gases released by heating throughout the system. Comparison of the TALMS signal with that obtained from direct injection indicates negligible losses because of trapping. An example of this approach that involved a different method of measuring the released benzene will be found in Section 3 under the heading "Cryogenic Trapping". The approach described here utilizes a simplier trapping procedure that is discussed in more detail in the appendix.

A convenient method of calibrating the TALMS instrument in the field is necessary to assure quality control. This method consists of recording the value of the TALMS signal when cells containing a fixed amount of benzene are inserted in the light path of the instrument. The cells are of different path length so that the TALMS signals will correspond to points well separated on the straight line portion of the analytical curve. Programs can be written so that the instrument may be calibrated by storing two values obtained with the two cells in the memory of the HP-85. Subsequent values, obtained when samples are introduced into the system, may now be stored (or printed out) in the same units used in the calibration procedure (e.g. ppm).

A fixed amount of benzene vapor may be maintained in the calibration cells with the arrangement sketched in Figure 30. It is necessary that all liquid or solid benzene in the cell be in contact with the ice bath, i.e. in the cold finger. Otherwise the vapor pressure will be very high and will fluctuate with the ambient temperature. When the liquid or solid benzene is at 0 ^{o}C the equilibrium vapor pressure is 24.5 torr [19]. Cells have been made by evacuating and sealing off while the benzene in the cell is held at liquid nitrogen temperature. If the instrument is to be used for samples at atmospheric pressure, the cells should be sealed off at about the same pressure. It is a simple matter to mount the cell and ice bath along the optic axis for instrument calibration.

A pressure effect of the type described earlier for phenol (Section 3) also occurs with benzene. In this case the TALMS signal decreases about 50 % as the pressure is increased from ca. 100 torr (0.013 MPa) to 760 torr (0.101 MPa). Line shape measurements at different pressures would reveal a quantitative explanation of this effect but it seems certain that it is caused by line broadening. Since the analytical curve in Figure 29 was obtained by injecting vapor into an evacuated cell, a correction is necessary if the cell is to be used at atmospheric pressure.

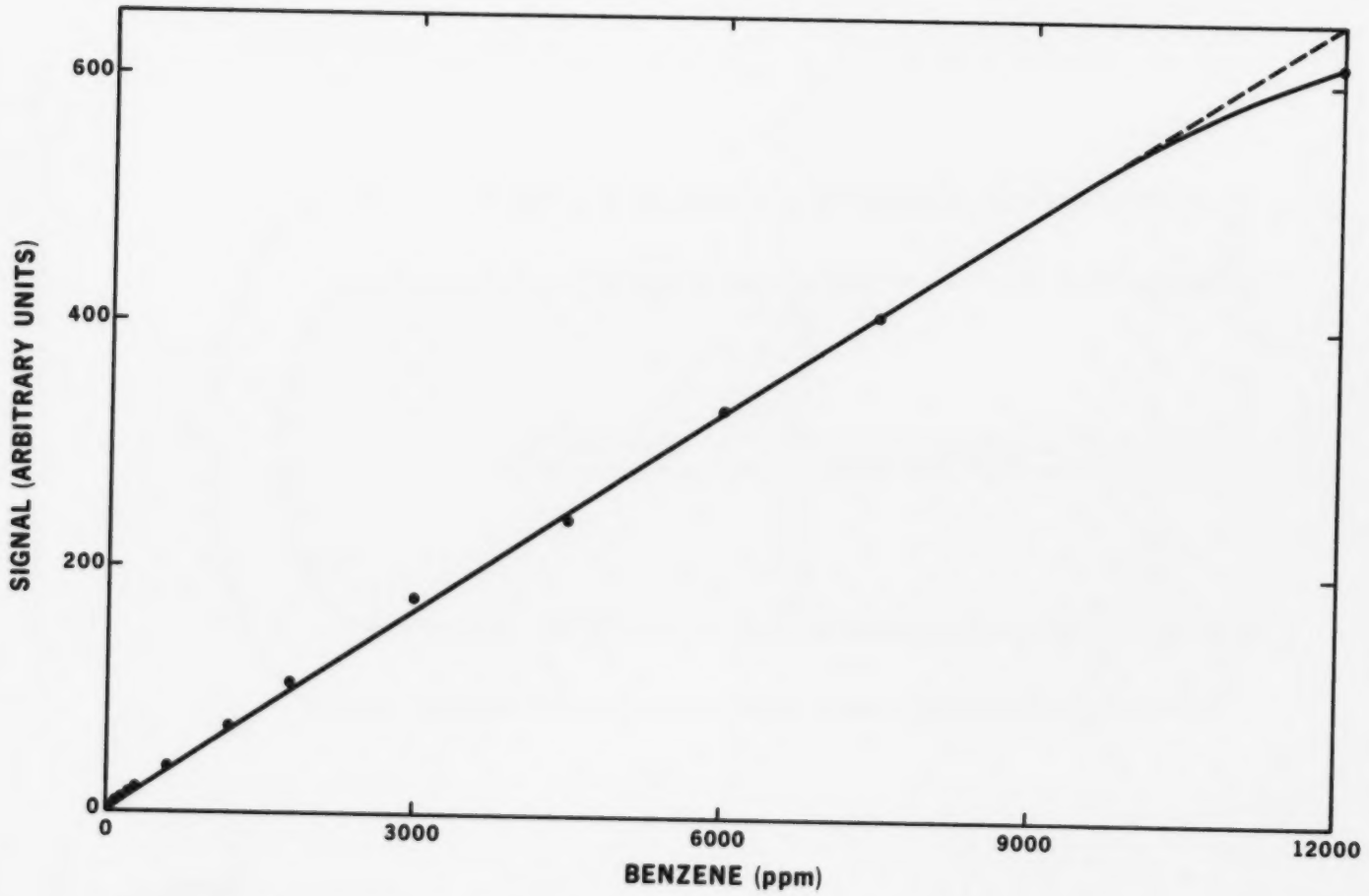
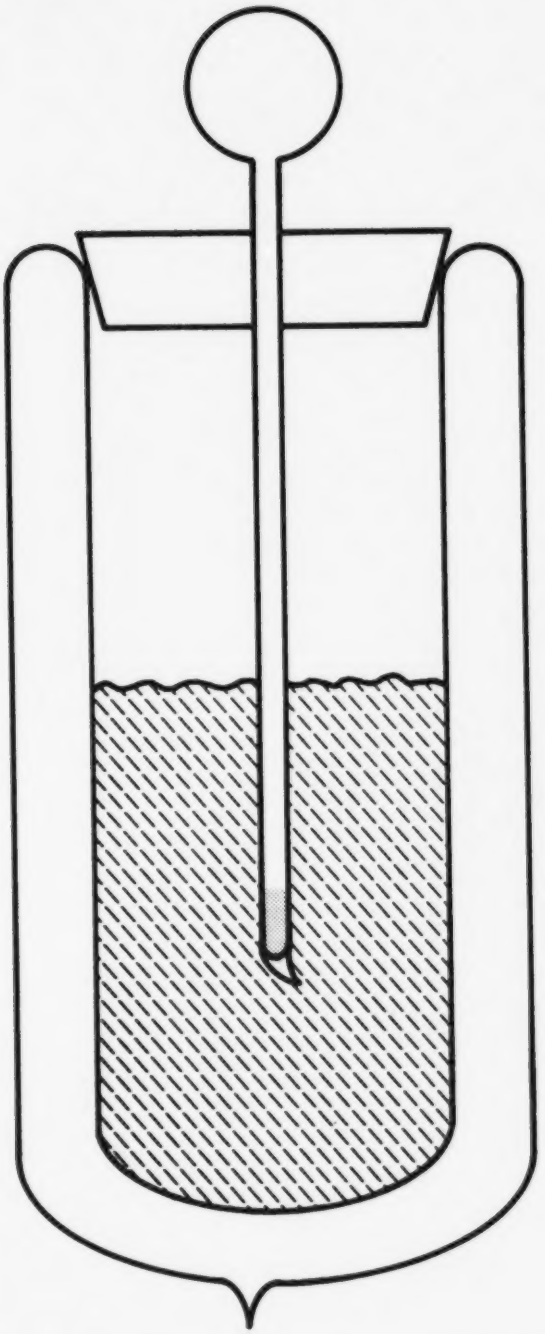


Figure 29. Benzene signal at 253.6 nm with a double beam TALMS.

XBL 833-8541



XBL 832-8470

Figure 30. Benzene field calibration cell.

Extensive testing for interference from other molecules should be carried out to verify instrument performance. An indication of this type of problem occurred when volumetric calibration of the instrument was attempted. Known volumes of benzene were dissolved in toluene and evaporated into the TALMS cell. This approach was discontinued because of indications that the toluene was responsible for a TALMS signal. If the observed effect is not due to impure toluene or some other artifact, the data indicate the system is thirty times more sensitive to benzene than to toluene. That is, if the two compounds were present in equal concentration, the measured benzene signal would be 3 % higher than the true value. These observations should be further investigated using high purity toluene. A particular monitoring need may dictate testing for interference from other molecules using this approach.

PHENOL AND FORMALDEHYDE

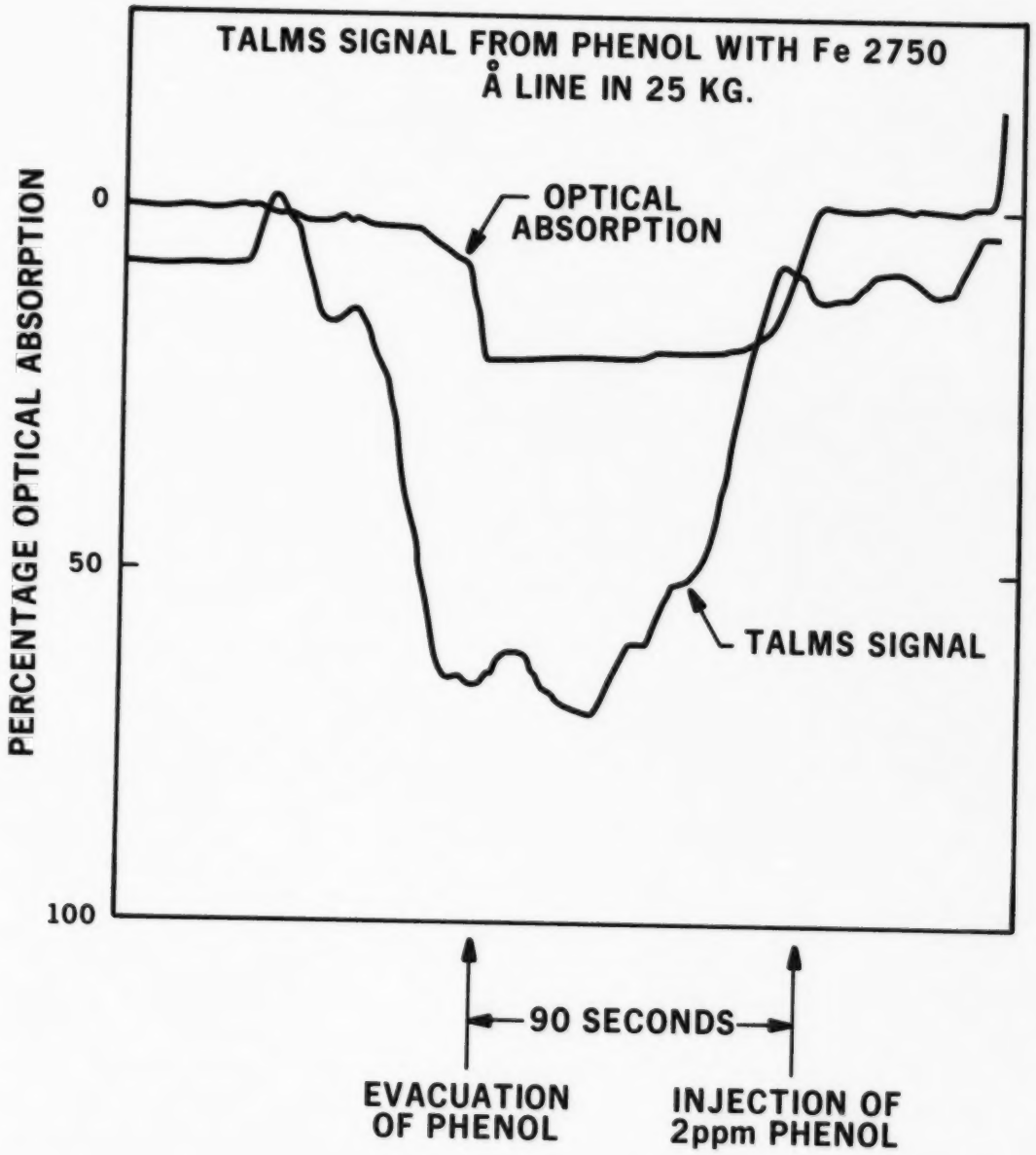
Detection of phenol and formaldehyde require different equipment than that used for benzene detection. A different light source is required and a monochromator is necessary to isolate the atomic lines used for the measurement. The analytical tests described here are included to demonstrate the application the TALMS technique to the detection of other compounds. Phenol detection was described in Section 3 under the heading "Atomic Line Selection". An approximation to the lower limit of detection (LLD) was determined by using a syringe to transfer a known volume of vapor in equilibrium with solid phenol into the absorption cell of a TALMS instrument. The following relationship between vapor pressure and temperature was used:

$$\log_{10} P = A - B/(C + t)$$

Where P = vapor pressure in torr
t = temperature in ^{o}C
A = 7.13617
B = 1518.1
and C = 175.0

This data was taken from "Lange's Handbook of Chemistry" [20]. Knowing the volume of vapor withdrawn, the vapor pressure of phenol, and the volume of the cell, it was possible to calculate the concentration in the absorption cell. The results of injecting vapor corresponding to 2 ppm of phenol are displayed in Figure 31. In this figure time increases from right to left. It takes something less than one minute for the sample to equilibrate by diffusion in the cell. The signal to noise ratio is ca. 6/1, implying a LLD of 1 ppm-v.

A similar experiment was carried out to determine the LLD of formaldehyde. The formaldehyde was injected into the cell by withdrawing vapor in equilibrium with an aqueous solution of formaldehyde. Vapor pressure, temperature and concentration, relationships reported by Ledbury and Blair were used to calculate the amount of formaldehyde in the cell [21]. A summary of vapor pressure and other formaldehyde properties has been authored by Walker



XBL 832-8368

Figure 31. TALMS signal with the 275 nm Fe line at 2.5 T (25 kG) and 2ppm-v phenol.

[22]. These data indicated the LLD to be ca. 1 ppm-v. However, it was later realized that the Ledbury - Blair work did not differentiate between various formaldehyde species in the vapor. Formaldehyde can exist as a polymer, a hydrate, or a hydrated polymer in the vapor phase. Hall and Piret [23] determined that only if the vapor were heated above 80 ^{o}C would formaldehyde be in the monomeric, dehydrated form. A furnace assembly that will allow the cell to be heated above this temperature is under construction so that more accurate calibration data for formaldehyde may be obtained.

REFERENCES

[1] T. Hadeishi, R. McLaughlin, and J. Millard, "Development of a Tunable Zeeman Spectrometer for Analysis of Toxic Organic Compounds", EPA 600/4-82-067, U. S. Environmental Protection Agency, Research Triangle Park, NC 1982.

[2] T. Hadeishi, H. Koizumi, R. D. McLaughlin, and J. E. Millard, "Tunable Atomic Line Molecular (TALM) spectrometer", Spectrochim. Acta, 37B(6), 501 (1982).

[3] D. R. Scott, H. Koizumi, T. Hadeishi, and R. McLaughlin, "High Resolution Study of the $^{r}R(K" = 3)$ Structure of the 3390 Å Formaldehyde Band", J. Molec. Spectros., 92, 272 (1982).

[4] H. B. Singh, L.J. Salas, A. J. Smith, and H. Skigeishi, Atmos. Environ., 15, 601 (1981).

[5] F. A. Jenkins and H. E. White, "Fundamentals of Optics", 3rd edition, McGraw-Hill Book Co., Inc., 1957.

[6] Hideaki Koizumi, Tetsuo Hadeishi, and Ralph McLaughlin, "A New Technique for the Determination of SO_2 by a Zeeman Shifted Atomic Line", Spectrochim. Acta, 36B(5) 483 (1981).

[7] D. A. Skoog and D.M. West, "Principles of Instrumental Analysis", 2nd ed., Saunders College/Holt Reinhart and Winston 1980.

[8] B. V. L'vov, "Atomic Absorption Spectrochemical Analysis", Adam Hilger Ltd 1970.

[9] G.F. Box and A. Walsh, Spectrochim. Acta 16 , 225 (1960).

[10] S. Flugge, Ed., "Encyclopedia of Physics", Vol. XXII, G. Francis, "The Glow Discharge at Low Pressure", Springer-Verlag, Berlin, Heidleberg, New York, 1956.

[11] ibid S.C. Brown, "Breakdown in Gases: Alternating Fields".

[12] G. H. Atkinson and C. S. Parmenter, J. Molec. Spectros., 73, 52 (1978).

[13] T. Hadeishi, R. D. McLaughlin, J. G. Conway and D. R. Scott, "Tunable Atomic Line Molecular Spectroscopy of Benzene: Signals with Hg 253.6 nm and Co 252.8 nm Lines", submitted to Anal. Chem., 1982.

[14] B. Vodar, "Spectroscopic Study of Intermolecular Forces in Gaseous Mixtures", Spectrochim. Acta 14, 213 (1959).

[15] Chem and Eng. News, June 8, 1981, pg. 31 et seq., ibid Oct 5, 1981, pg. 13.

[16] J. Christoffensen, J.M. Hollas, and G.H. Kerby, Proc. Roy. Soc. A307, 97 (1968); J. Molec. Spectros. 24, 402 (1967); ibid, 24, 413 (1967).

[17] G.A. Eiceman and F.W. Karasek, "Retention Behavior of Chlorinated Benzenes, Chlorinated Phenols, Aldrin, and Aroclor 1242 on Tenax-GC, Chromosorb 101, Florisil, and Carbopack C HT", J. Chromat., 200, 115 (1980).

[18] R.D. Cox, M.A. McDevitt, K.W. Lee, and G.K. Tannahill, "Determination of Low Levels of Nonmethane Hydrocarbons in Ambient Air", Environ. Sci. Technol., 16, 57 (1982).

[19] "Handbook for Chemistry and Physics", 61st ed., Chemical Rubber Co. Press, 1980-1981.

[20] J.A. Dean, ed., "Lange's Handbook of Chemistry", 11th edition, McGraw Hill, New York, NY 1973.

[21] W. Ledbury and E.W. Blair, "The Partial Formaldehyde Vapour Pressure of Aqueous Solutions of Formaldehyde", J. Chem. Soc., London 127, 2832 (1925).

[22] J. F. Walker "Formaldehyde", 3rd ed., American Chemical Society Monograph Series, Reinhold Publishing Corp., 1964.

[23] M.W. Hall and E.L. Piret, "Distillation Principles of Formaldehyde Solutions: State of Formaldehyde in the Vapor Phase", Indust. Engr. Chem. 41(6), 1277 (1949)

APPENDIX A

INSTRUCTION MANUAL FOR

TUNABLE ATOMIC LINE MOLECULAR SPECTROMETER

December 7, 1982

This is a preliminary operations manual for the Tunable Atomic Line Molecular Spectrometer (TALMS) Benzene Monitor. This manual describes the components of the Benzene Monitor, and provides the necessary information to make proper cable connections, and to tune the instrument for operation.

Description of the Benzene Monitor Components

Light Source

The light source is a Pen Ray Mercury discharge lamp (2.125 inches long, 0.25 inches in diameter). The lamp is mounted in a Varian flange in a 0.3 inch gap between the pole tips. The light is passed through a collimator in which is mounted a 50 mm focal length lens. The light source and housing are mounted in a permanent magnet producing a field strength of about 7 kilogauss between the pole tips.

Polarization Compensation Plate

The polarization compensation plate is a quartz glass plate mounted so that it can be rotated and secured at any angle to the light beam.

Variable Phase Retardation Plate

The variable phase retardation plate is also known as the squeezer and will be referred to as such throughout the remainder of this report. It is a quartz plate mounted between the arms of a C electromagnet in a black plastic housing.

Beam Splitting Assembly

The primary component of the beam splitting assembly is a partially reflecting mirror. It is a one inch square quartz glass plate that has been coated with Aluminum so that it will reflect 37% and transmit 37% of 450 nm light at a 45 degree incidence angle. The mirror is mounted in a Varian 1.5 inch O.D. tee. The mirror can be rotated by turning the grey knob at the top of the assembly. The angle of the mirror can be locked by tightening the nut at the base of the knob.

The entrance to the straight section of the beam splitting assembly is a collimator with a 50 mm focal length focusing lens. Behind the lens is a linear polarizer. The orientation of the polarizer can be adjusted through the slot cut in the collimator. The set screw secures the polarizer in a fixed position. The sample cell attaches to the other end of the straight section. A 100 mm focal length focusing lens is mounted here to pass light through the sample cell. A Hamamatsu R166 photomultiplier tube is mounted on the right angle section of the assembly. A 50 mm focal length focusing lens is mounted in the flange between the photomultiplier tube and the Varian tee.

Sample Cell

The sample cell is a Varian 1.5 inch diameter tube with one inch diameter quartz glass windows mounted on each end. The path length is 6.4 inches (164 mm) and the volume is 134.1 cubic centimeters. The sample entrance and

exit tubes are at each end of the cell. The stainless steel valves are not mounted on the sample cell, rather they are mounted on the track of the instrument base so that they can be opened and closed without shaking or moving the sample cell and beam splitting assembly. The entrance to the sample cell is attached to the beam splitting assembly. A Hamamatsu R166 photomultiplier tube is attached to the exit of the sample cell. A 50 mm focal length focusing lens is mounted in the flange between the sample cell and the photomultiplier tube.

Photomultiplier Tube

Both photomultiplier tubes are Hamamatsu R166 solar blind tubes. Their range of response is 160 to 320 nm. Because of this response there is no need for a bandpass filter to isolate the 253.6 nm monitoring line. The photomultiplier tube attached to the sample cell receives light that generates the TALMS signal and is called PMT 1. The photomultiplier tube attached to the beam splitter assembly receives light used to correct for light source fluctuations and drift. It is called PMT 2.

Each photomultiplier has a short BNC cable connected between the PMT signal output and a high frequency filter. The BNC cables for each of the PMTs must be the same length. The high frequency filters are in small blue Pomona boxes mounted to the optical light track on the base.

Instrument Base and Power Supply

The TALMS optical components are all mounted on an optical light track attached to a base. On the left side of the base is a cable track with three 3-pin Bendix connectors and one high voltage BNC cable. The high voltage BNC cable supplies power to the Light Source. The connector interface between the lamp cord and the BNC cable is in a small blue Pamona box that fits underneath the magnet. Two of the 3-pin Bendix terminals are labeled 1 and 2 and they are connected to the high frequency filters for PMTs 1 and 2 respectively. Two of the pins supply + and - 15 volts to the high frequency filter. The third pin carries the PMT output signal. The third 3-pin connector supplies power to the squeezer. Although the connectors for the squeezer and PMT 2 are close together, it is not possible to mix them up because one is a male connector and the other is a female connector.

The power amplifiers for the squeezer and the light source and the DC power supplies are mounted in a drawer in the base. The drawer is secured by two screws on the end panel. The drawer can be completely removed for servicing if necessary.

In order to pull this power supply drawer out of the base it is necessary to disconnect 5 cables. Three of the cables connect to the back side of the end panel. Two of these are BNC cables labeled "power in" and "current". The third is a grey cable with a 3-pin Bendix connector attached to a blue Pomona box. This carries the photomultiplier tube outputs to the NIM Bin. The other two cables are connected to the terminal bar on the left of the power amplifiers with spade lugs. One of these cables connects to two

terminals labeled "0-8 volts" and "output B". The order in connecting the two wires does not matter. The other cable connects to two terminals labeled "+ 15 v" and "- 15 v". The order in connecting the wires does matter and is labeled on the cable.

After all five cables have been disconnected the drawer will slide out until it reaches the slide stops. Lift drawer slightly to get over the stops and pull out completely. The transformer for the light source is mounted separately on the base behind the power supply drawer. It is accessible from the other end of the base by removing the protective screen from that end.

Description of NIM Bin and Components

There are 5 NIM Bin modules needed to operate the TALMS instrument. These electronic modules should be kept together and not mixed with other existing TALMS instrumentation. A description of each module is given below. Wiring schematics for each module are provided at the end of this manual.

PMT Module

The PMT Module supplies high voltage power to both photomultiplier tubes.

Front Panel - There is an on/off switch and voltage level control knob for each PMT. The labels "PMT 1" and "PMT 2" on the front panel correspond to the outputs labeled "PMT 1" and "PMT 2" on the rear panel

Rear Panel - The high voltage outputs for PMT 1 and PMT 2 are to be connected to the appropriate photomultiplier tube using the black high voltage BNC cables.

Squeezer Module

The Squeezer Module contains an audio frequency generator that provides the reference signal to the lock-in-amplifier and the AC signal to the squeezer power amplifier in the base of the TALMS monitor. The DC voltage control for the squeezer is also in this module

Front Panel - The meter on the front panel measures current to the squeezer. The knob labeled "variable" controls the current to the squeezer. The knob labeled "gain" varies the amplitude of the AC signal from the frequency generator that controls the AC power to the squeezer. The frequency is adjusted with the potentiometer labeled "freq".

Rear Panel - The BNC output on the top of the rear panel supplies the reference signal to the lock-in-amplifier and is to be connected to the "ref. in" input on the rear panel of the lock-in-amplifier. It can also be used as a trigger source for an oscilloscope. The bottom BNC output is to be connected to the TALMS monitor end panel at "Input B".

Light Driver Module

The Light Driver Module provides the high frequency driving signal to the light source power amplifier in the base of the TALMS monitor.

Front Panel - The potentiometer on the front panel labeled "frequency" varies the frequency of the signal to the power amplifier. The knob labeled "amplitude" varies the amplitude of the signal to the light source power amplifier. The amplitude knob can be locked by tightening the nut on the base of the shaft.

Rear Panel - The BNC connector labeled "output" is to be connected to "Input A" on the end panel of the TALMS monitor. The BNC connector labeled "current" is to be connected to "current" on the end panel of the TALMS monitor.

Dual Beam Tracking Module

The Dual Beam Tracking Module (DBTM) accepts the input from PMT 1 and PMT 2. Each signal is passed through a logarithmic amplifier and then one signal is subtracted from the other in a difference amplifier.

Front and Rear Panel - "Input 1" and "Input 2" on the module is to be connected to the BNC connectors on the back panel of the NIM Bin mainframe. They are labeled "1" and "2". The output labeled "AC diff output" is to be connected to the lock-in-amplifier input labeled "sig in". The outputs labeled "buffer" are used to monitor the PMT signals before going through the log amplifier. The outputs labeled "log out" are used to monitor the PMT signals after going through the logarithmic amplifier.

On the front panel is a switch labeled "Ch. 2 log amp on/off". This is to be kept in the "on" position for normal operation. The off position is to be used when inserting external sample cells in the light beam for calibration purposes.

Lock-in-amplifier Module

The lock-in-amplifier uses phase locked detection to extract the squeezer modulated signal from the photomultiplier tubes and provides a DC voltage output proportional to the sample concentration in the cell.

Front Panel - To monitor signals in the lock-in-amplifier use the connector under the knob labeled "Monitor".

Rear Panel - Connect "ref in" to the top BNC connector on the squeezer rear panel. Connect "sig in" to the "AC diff output" on the Dual Beam Tracking Module rear panel. Connect "output" to the "input" on the Time Constant Module.

Time Constant Module

The Time Constant Module will average the input signal over a given time interval.

Front Panel - The selector knob selects 1, 10, 30, 50, and 100 second time averaging intervals. The button labeled "zero" will null the circuit in the module to begin averaging again. The "adjust" knob will add a DC offset to the output. The "input" and "output" can be connected through the front panel.

Rear Panel - The "input" is to be connected to the "output" on the rear panel of the lock-in-amplifier. The "output" is to be connected to a data collection device (e.g. a strip chart recorder).

Connections between the TALMS Monitor and the NIM Bin

The 19-pin connector and the two 3-pin connectors and cable are to be connected between the TALMS monitor base and the NIM Bin mainframe back panel. There should be no confusion here since all three connectors are different. The input "power in" on the end panel is connected to "output A" that is also on the end panel. The input "current" on the end panel is connected to "current" on the Light Driver Module. The "input A" is connected to "output" on the Light Driver Module. The "input B" is connected to the bottom BNC connector on the rear panel of the Squeezer Module. The inputs "spare" and "0-8 v" have no connections. The AC power cord is plugged into the endpanel of the TALMS monitor (use 120 volts AC power)

Operating Instructions

The switch on the right hand side of the front of the NIM Bin mainframe switches on power for both the NIM Bin and the TALMS monitor. After all connections have been made between the modules, the NIM Bin, and the TALMS Monitor, turn the instrument on.

Step 1.

Make sure the light source is on. If not adjust the amplitude and frequency on the Light Driver Module.

Step 2.

Remove the Polarization Compensation Plate or turn it perpendicular to the light beam. Turn on PMT power to both phototubes. Make sure the light beam is reaching PMT 1. Set voltage on PMT 1 so that the output from the Dual Beam Tracking Module buffer for PMT 1 is about -3.0 volts. Adjust the mirror in the Beam Splitter to get maximum output from PMT 2. Set the voltage on PMT 2 so that the output is about -3.0 volts.

Step 3.

Monitor the buffer outputs on the DBTM for PMT 1 and PMT 2 on an oscilloscope. Look for an AC signal at about the 50 mv/cm gain setting. Adjust the AC and DC controls on the Squeezer Module until the maximum undistorted sine wave is obtained from PMT 1 and PMT 2. Adjust the PMT voltages so that the sine wave signals from both PMTs overlay exactly.

Step 4.

Turn the ch-2 PMT power off. Connect the oscilloscope to the "monitor out" jack on the lock-in-amplifier. Set the monitor knob to "ref" and adjust the reference frequency knob to get a maximum sine wave consistent with good wave form. Set the knob to "sig" and tune the sine wave signal to maximum. Set the knob to "mix" and adjust the phase control to full wave rectified form. Now turn the ch-2 power back on and allow the system to stabilize.

Step 5.

Adjust the Polarization Compensation Plate so that signals from the buffer outputs of the DBTM are no longer sine waves but are now just straight line signals.

Step 6.

Set the meter on the lock-in-amplifier to the 1 volt scale. Set the potentiometer to zero the meter. Set the gain and time constant as desired. Set the time constant on the Time Constant Module as desired.

Comments on Operation of the TALMS Monitor

In Step 3 in the Operating Instructions the PMT signals were adjusted to be exactly the same. In order for the reference signal tracking to work properly this condition must be maintained. The critical component in the TALMS monitor that can disturb this condition is the beam splitting mirror. Once set the mirror should not be moved. It was mentioned previously that the mirror orientation can be locked by tightening the nut at the base of the knob on the Beam Splitting Assembly. It is also critical that the whole assembly, including the mirror, not be moved relative to the light beam. This is the reason for mounting the sample cell valves on the light track. In this position the operator will not shake the mirror when opening and closing the valves which tend to stick when closed too tightly.

Calibration Procedures

A Benzene standard is prepared by cooling a flask of Benzene to 0 ^{o}C. A known volume of vapor from this flask is then injected into the sample cell using a gas tight syringe. This is usually done by evacuating and closing off the cell, inserting the syringe through a septum and allowing the vacuum to suck the vapor into the cell. The concentration of Benzene in the cell in part per million (ppm) is calculated from:

$$\frac{\text{(syringe vol. in } \mu\text{l)(24.468 mm Hg for Benzene at } 0^{o}\text{C)}}{\text{(0.1341 l cell vol.)(atm press in mm Hg)}}$$

To maintain an equlibrium state in the cooled flask, the benzene vapor should be withdrawn only after exhausting the syringe and filling it with the equlibrium mixture several times. This prevents a negative pressure from developing inside the flask and minimizes temperature differences between the vapor in the syringe and the vapor in the flask. If this procedure is followed temperature corrections, usually, will not be necessary. Some care must be taken when calibrating over a large dynamic range. There is a decrease in the TALMS signal with an increase in pressure. Injecting 40-50 cc of benzene calibration vapor may increase the pressure in the cell sufficiently to decrease the signal and cause a roll off from the linear calibration curve. Making all measurements at atmospheric pressure would solve this problem.

Operation Using the Cryogenic Trap

The procedure for testing the cryogenic trap operation will illustrate atmospheric sampling. In order to follow the procedure outlined below refer to the Figure A-1 titled "Cryogenic Trap Experimental Arrangement".

Step 1.

The inlet and outlet of the trap are wound with a heating coil to prevent ice accumulation at these points. Turn on the power to this coil. Close valve 1 and valve 2 and immerse the trap in a liquid nitrogen bath up to the inlet port. Allow about 5 minutes for the trap to cool.

Step 2.

The airflow should be set up as is shown in the figure. Open valves 1, 2 and 3 and turn on the pump. Set the flow to about 7.5 liters/minute.

Step 3.

Inject a known volume of benzene vapor into the trap inlet at valve 1. Monitor the TALMS signal to see if benzene has passed through the trap. The time constant should be about 10 seconds or less for this test. No benzene should pass through. If benzene has passed through, either the flowrate is too fast or the trap has not cooled sufficiently. If a TALMS signal is observed the trap must be blanked and the experiment begun again.

Step 4.

Close valve 1 and remove the trap from the liquid nitrogen bath. Evacuate the sample cell and the trap. At this point it may be desired to allow the trap to warm slightly to allow the liquid oxygen to escape. Two or three minutes with the liquid nitrogen trap removed and evacuated pressure should be sufficient. The TALMS signal will indicate whether any benzene escapes from the trap.

Step 5.

Close valve 2 and heat the main body of the trap to less than 100 ^{o}C.

Step 6.

Close valve 3 and open valve 2 and observe the benzene signal on the TALMS monitor. Open valve 1 to bring the pressure in the system to atmospheric. Close valve 1 and record the signal.

Step 7.

Pump the benzene out of the sample cell and the trap.

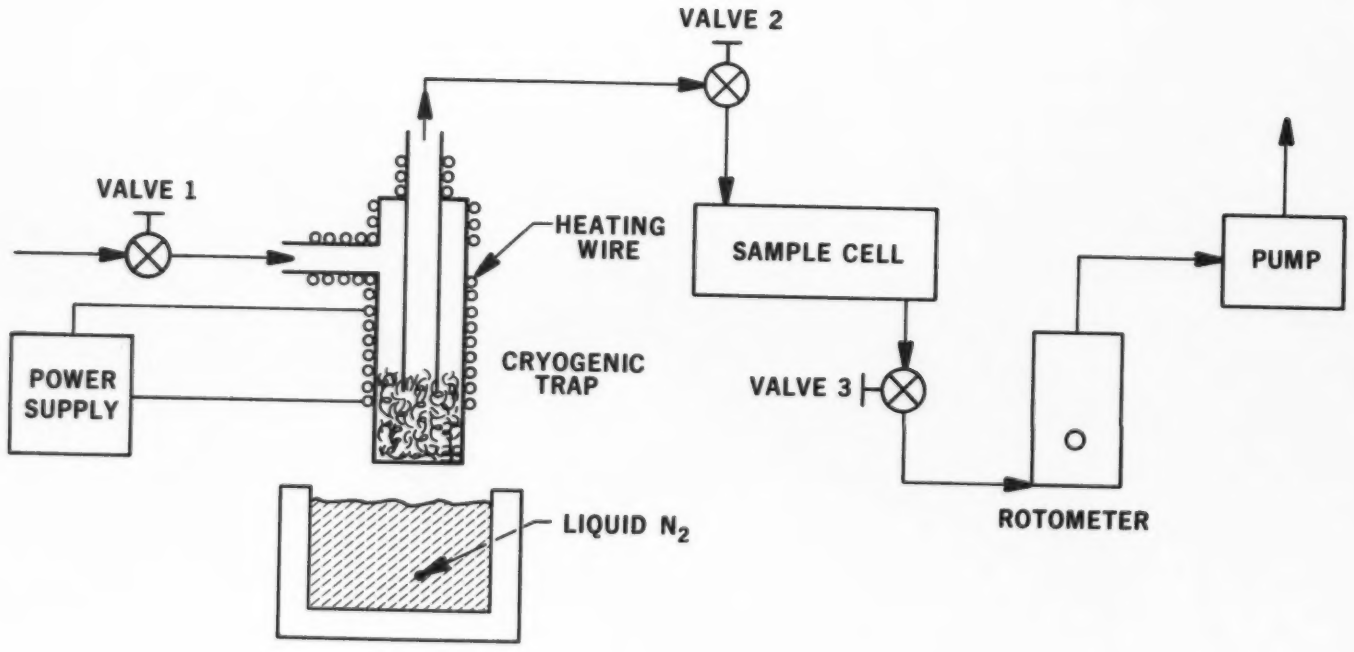


Figure A-1. Cryogenic trap, experimental arrangement.

Injection of the Calibration Sample

This calibration procedure is carried out with the trap at room temperature. The point of the procedure, outlined below, is to move the benzene through the system in exactly the same manner as the samples caught in the cold trap.

Step 1.

Close valve 1 and evacuate the trap and the sample cell. Close valves 2 and 3.

Step 2.

Inject a known volume of benzene containing vapor into the trap through valve 1. Close valve 1.

Step 3.

Open valve 2 and observe the benzene signal on the TALMS monitor. Open valve 1 to bring the system to atmospheric pressure. Close valve 1 and record the signal.

Step 4.

Pump the benzene out of the sample cell and the trap.

Follow the same procedure to obtain more calibration points.

Comments on Using the Cryogenic Trap

The time necessary to cool the trap down as well as that necessary to remove the liquid oxygen will have to be determined by experience. During both of these procedures the exit to the trap is open to the sample cell of the TALMS monitor so that any escape of benzene can be determined.

The purpose of eliminating the liquid oxygen and leaving the bulk of the water behind is to minimize the pressure in the system upon heating and to allow for the greatest movement of the trapped benzene into the sample cell. This also brings the procedure closer to the conditions present during the injection of calibration gas.

This trapping system was tested by inserting 5 cc of vapor containing benzene in equilibrium with the solid at ^{o}C. This provides a TALMS signal far above the lower limit of detection.

APPENDIX B

CIRCUIT DIAGRAMS

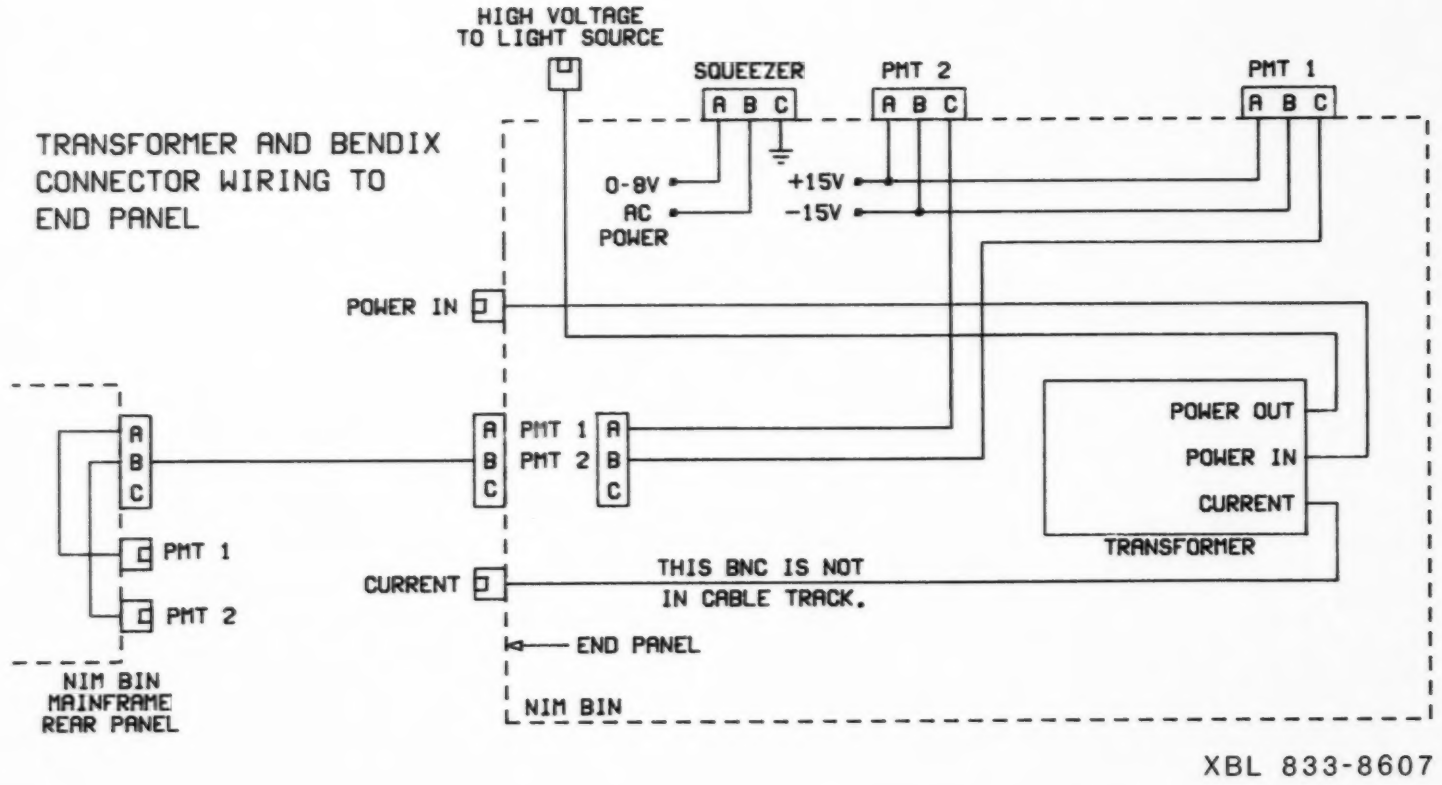


Figure B-1. Transformer and Bendix connector wiring to endpanel.

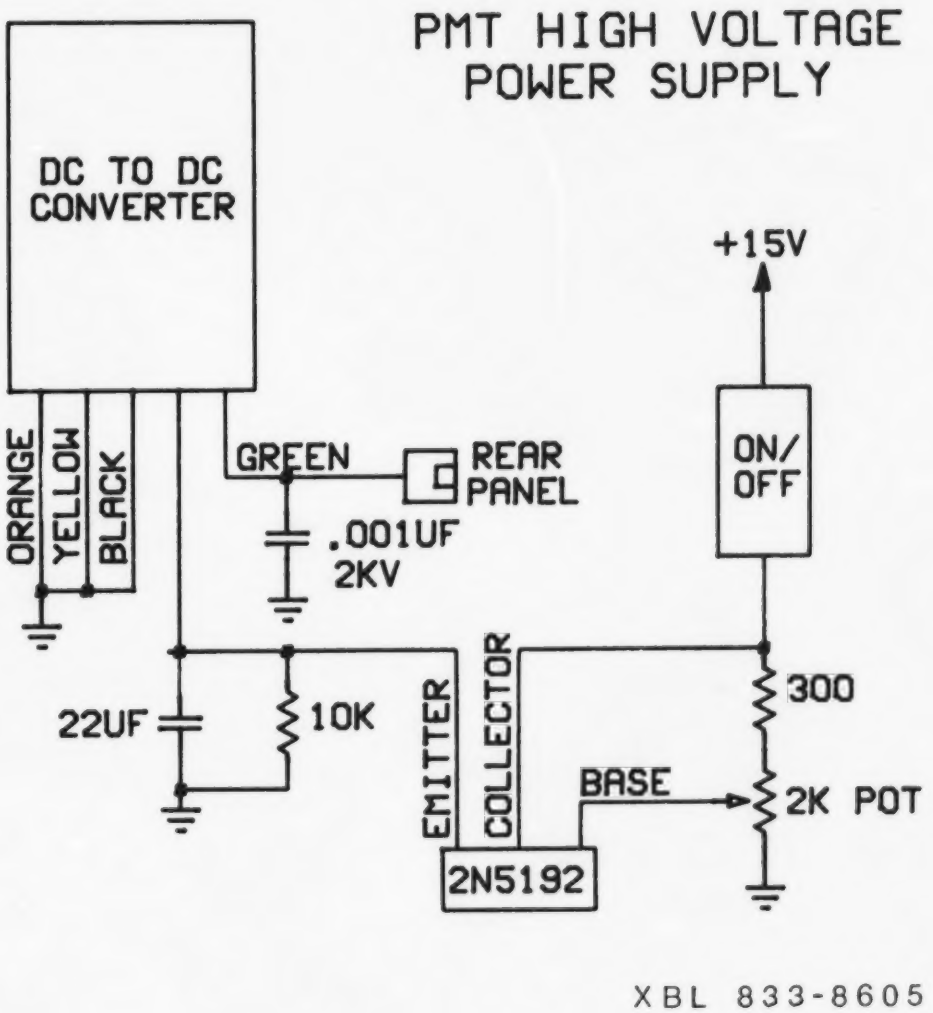


Figure B-2. Photomultiplier tube high voltage power supply.

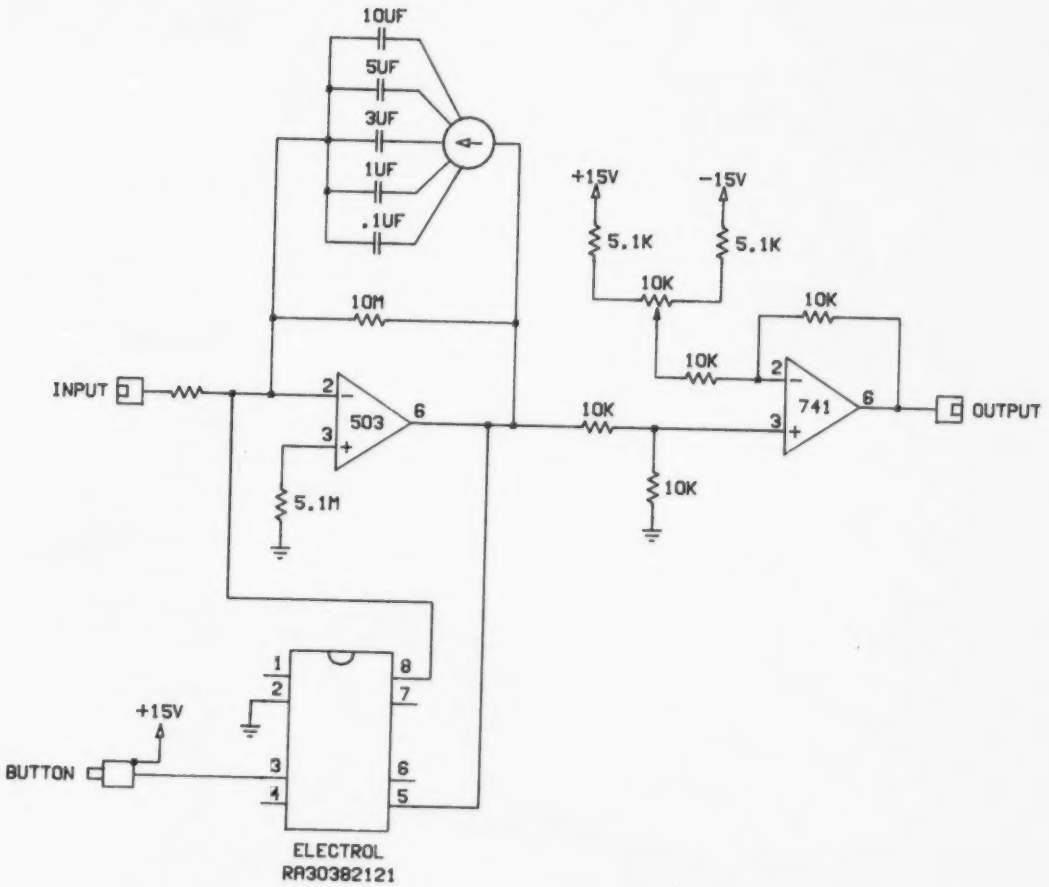


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Figure B-3. Time constant module.

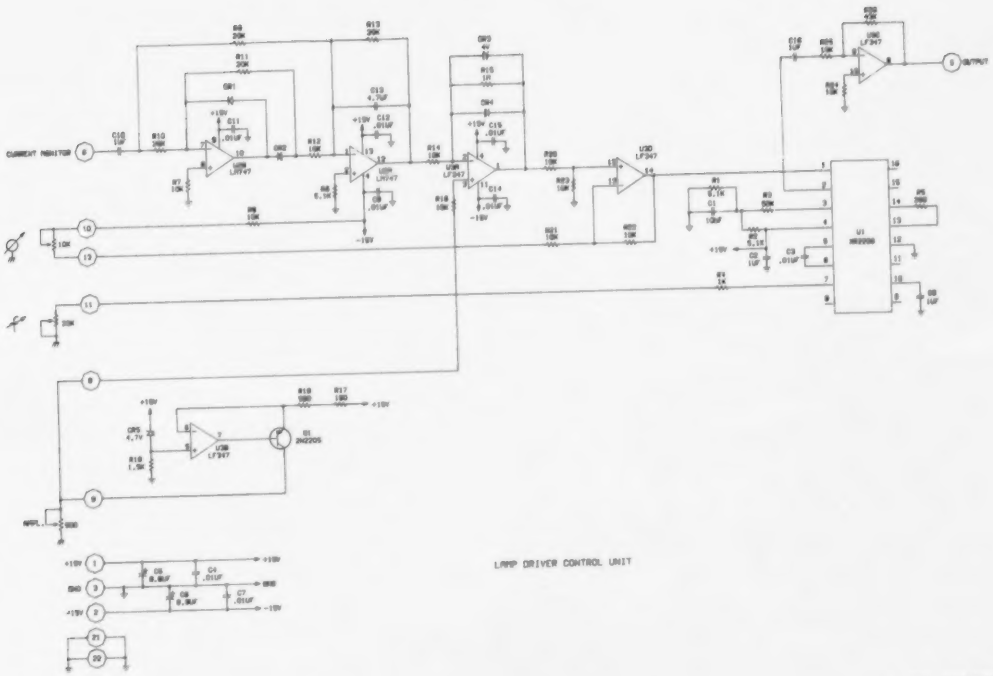

Figure B-4. Lamp driver control unit.

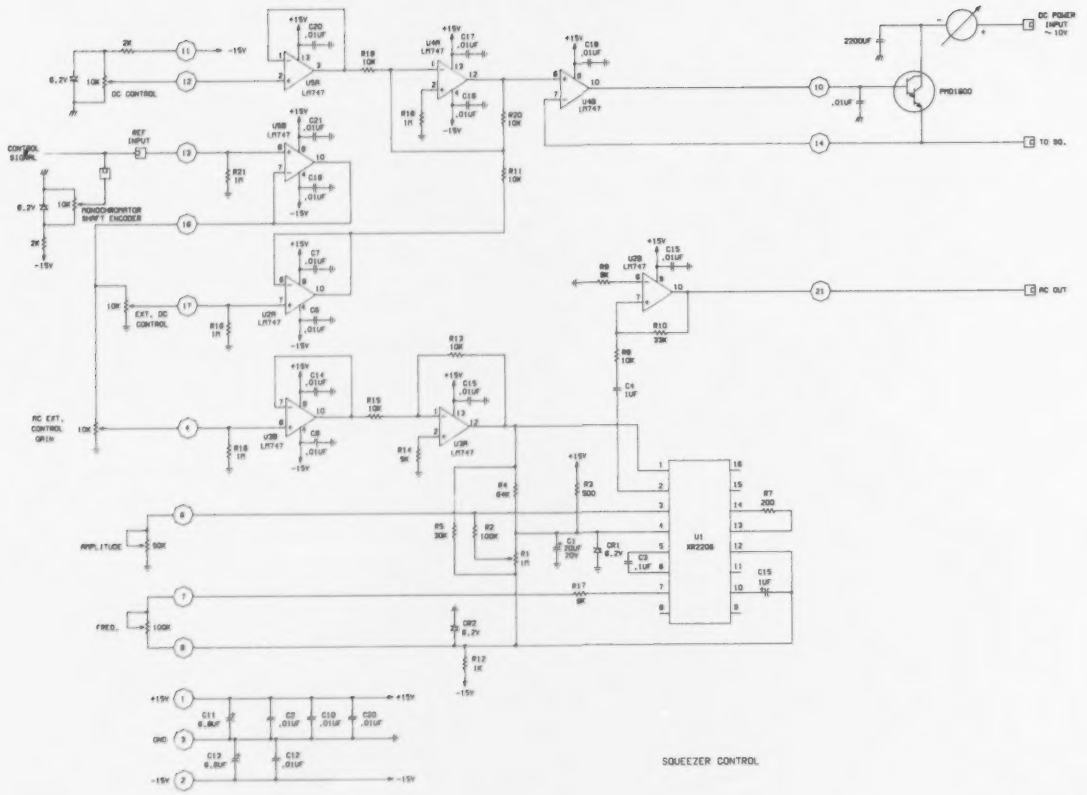

Figure B-5. Squeezer control.

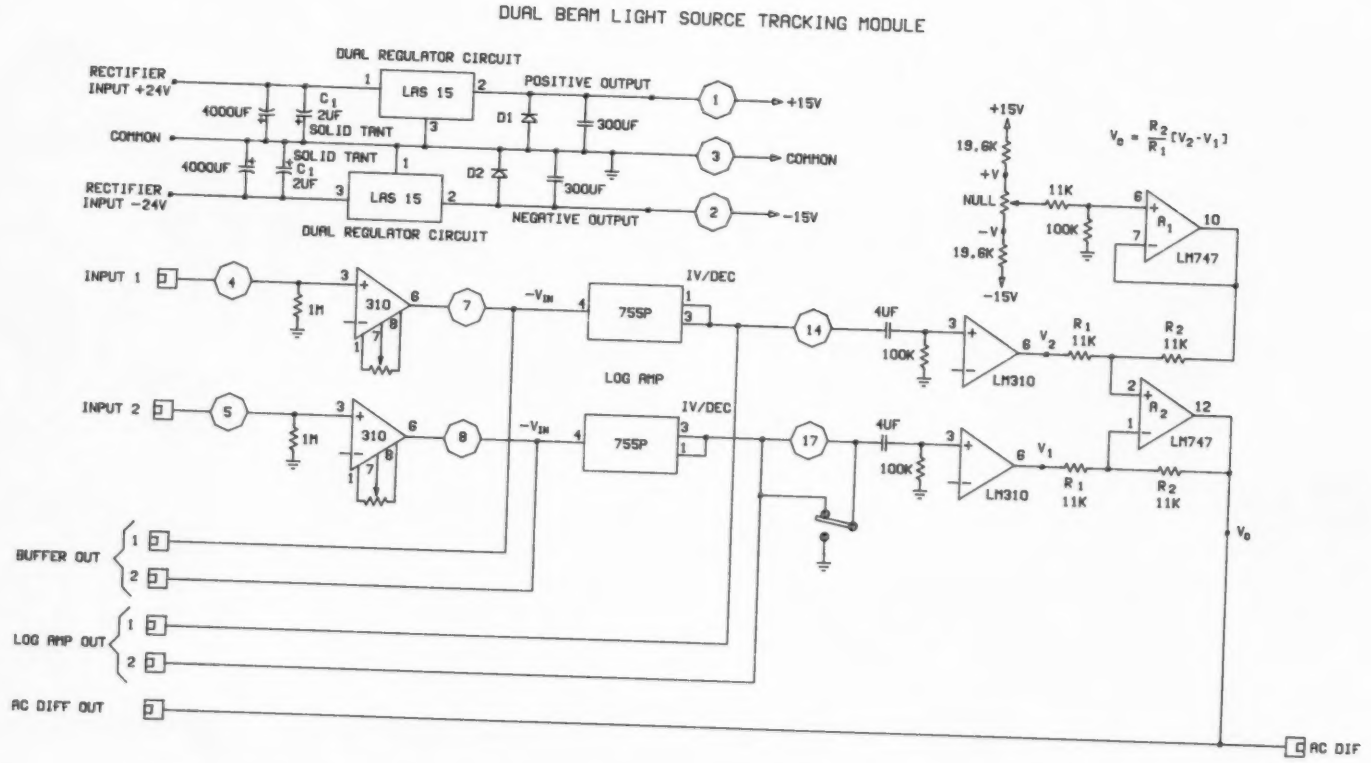

Figure B-6. Dual beam light tracking module.

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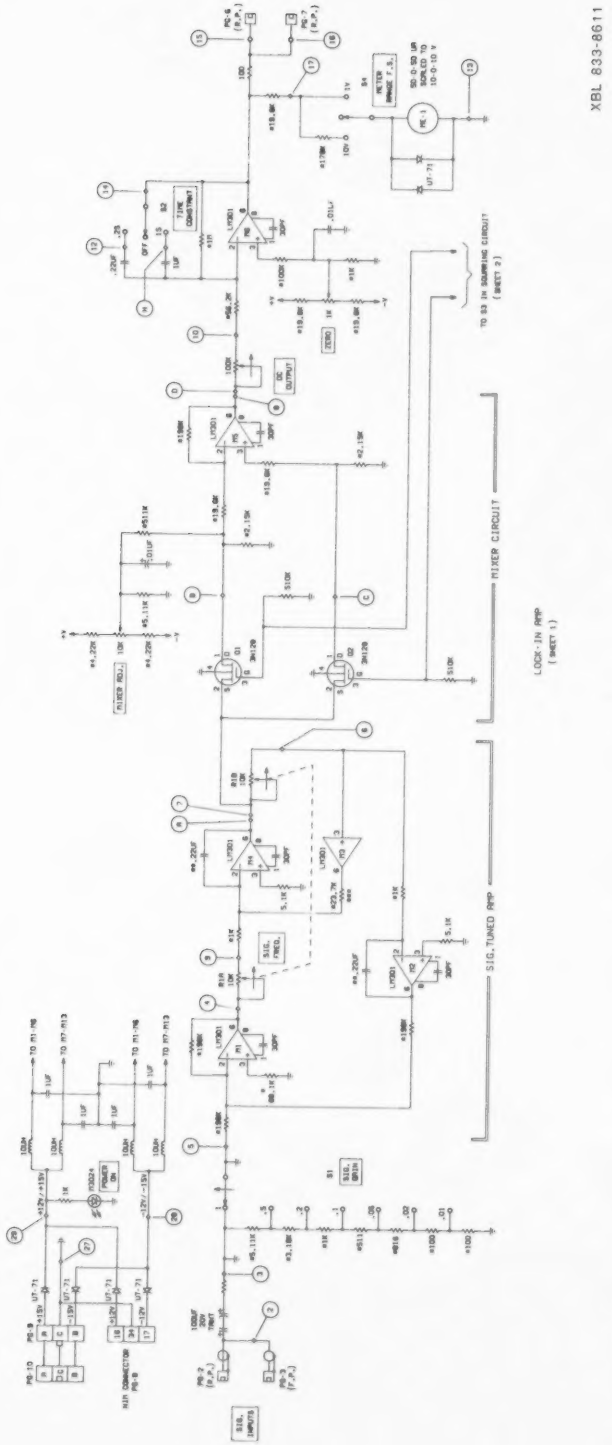

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Figure B-7. Lock-in amplifier.

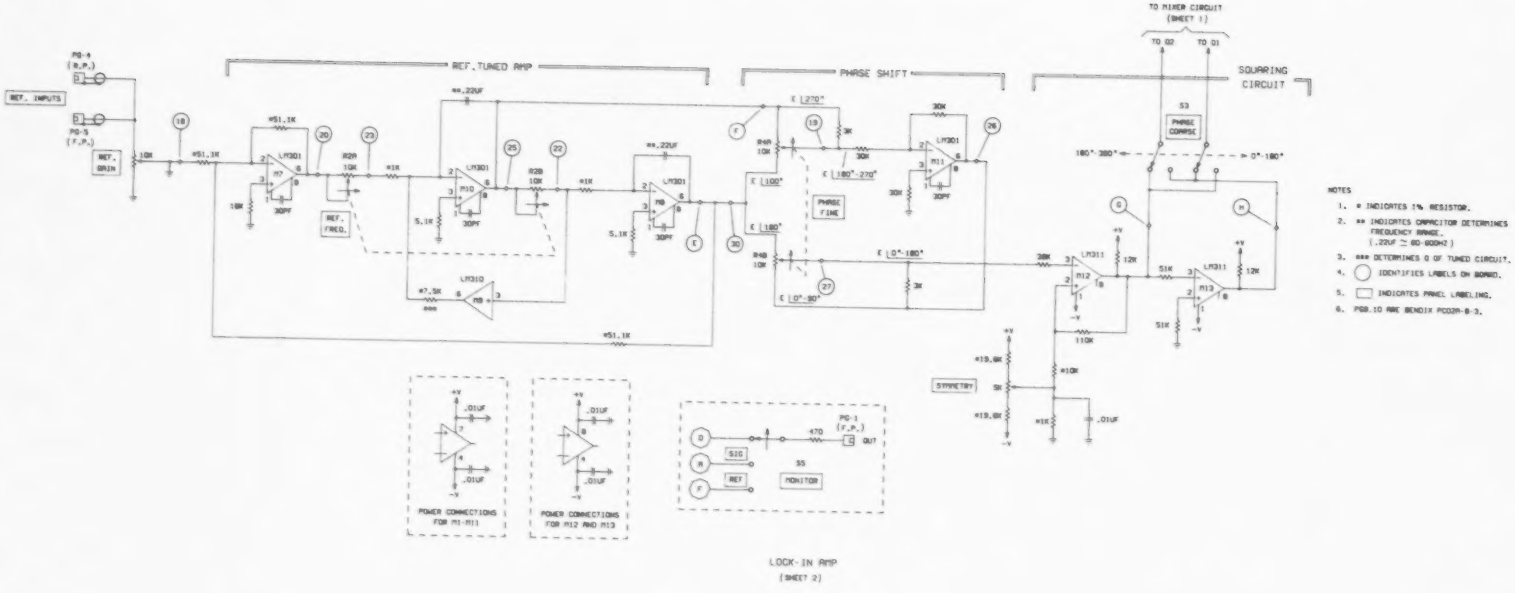

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Figure B-7. Continued

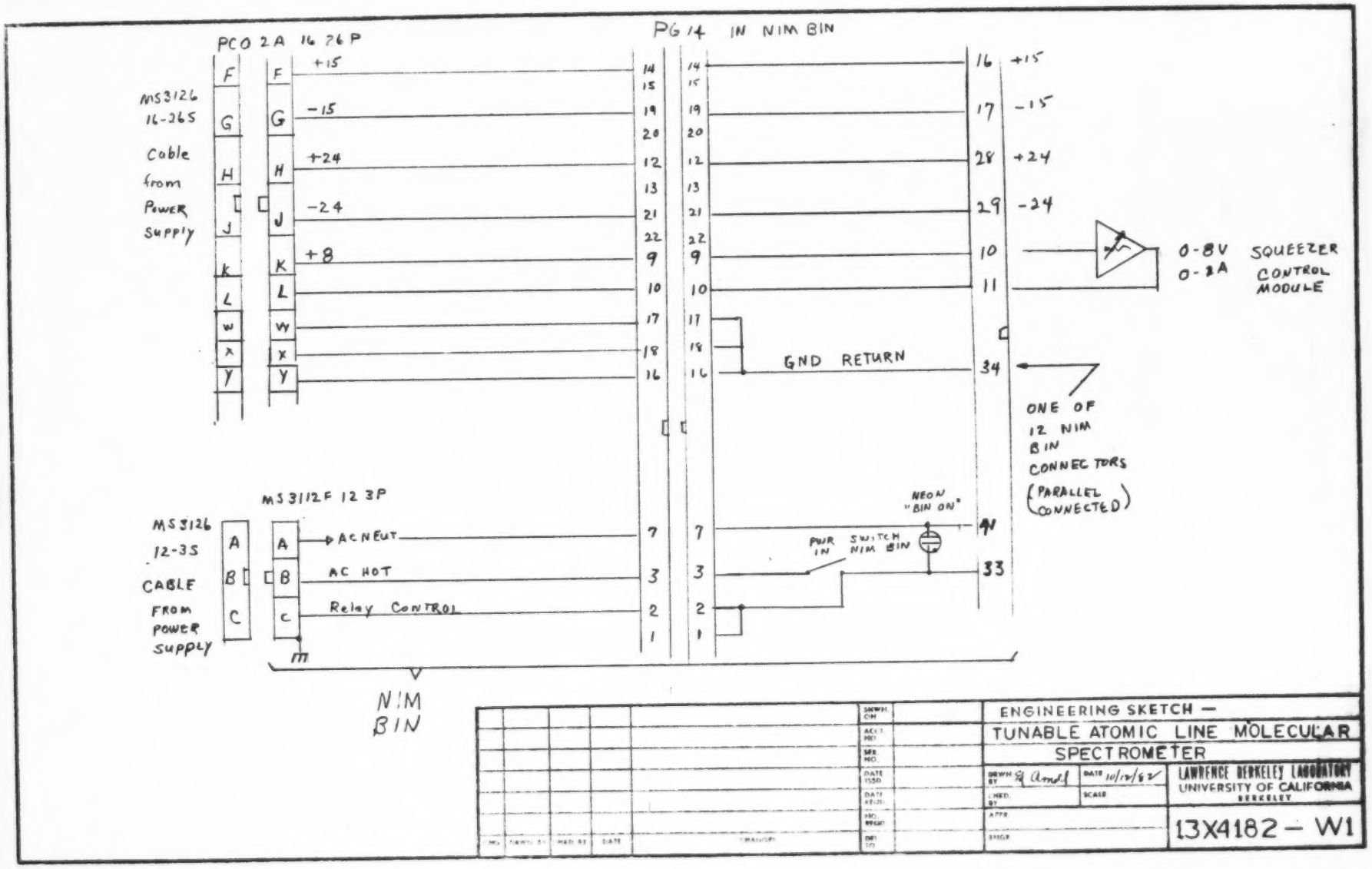

Fig B-8 Cable connections.

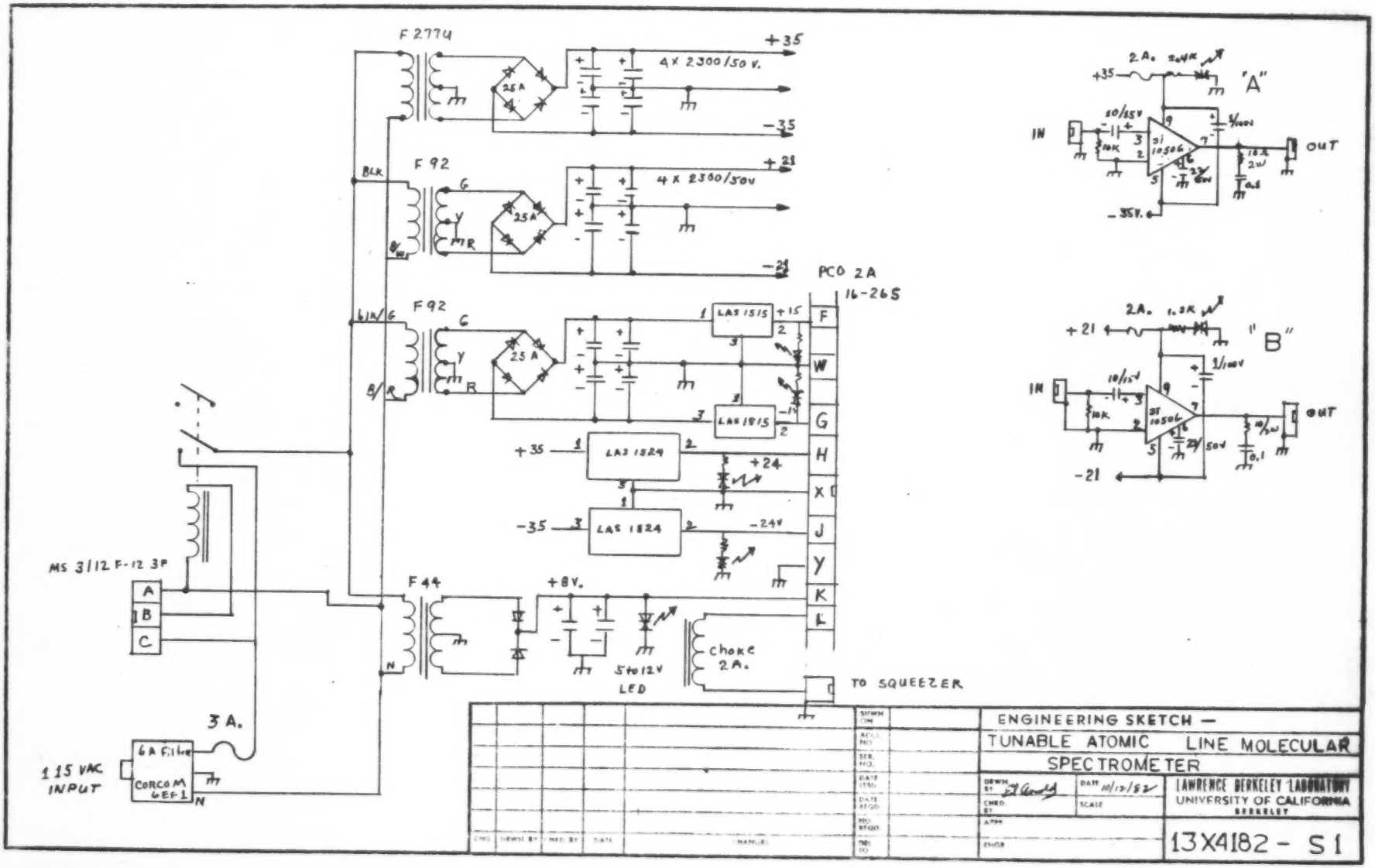

Fig. B-8 Cable connections (continued)